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Raman Spectrum of Benzene Under High Dispersion and the Isotope Effect

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The Raman spectrum of benzene has been photographed using a fine slit and a high dispersion glass Littrow spectrograph. The faint companion at 984 cm^{-1} is found to possess an intensity ratio of 6 : 100 when compared with the principal Raman line at 992 cm^{-1}. The view that this satellite arises from a benzene molecule in which one of the carbon atoms is replaced by the heavier isotope of atomic weight 13 is supported by this result. The distribution of intensity in the 3048 and 3062 Raman lines has been determined and the contours of the lines are drawn separately. The peaks of these two lines are found to be in the ratio of 1 : 1.35. The relatively sharp nature of 3062 and the diffuseness of 3048 are correlated with the facts that the former is a well-polarized Raman line whereas the latter is a fully depolarized line.

INTRODUCTION

THE author is engaged in a systematic study of the fine structure exhibited by the various Raman lines under high dispersion and some of the results obtained with benzene are of special interest as they confirm the recent findings of Cheng, Hsueh and Ta-You Wu.[1] The results given in this paper relate to the 992 and 3060 Raman lines of benzene and are obtained independently by the author during the course of a more extensive investigation. They are now reported here in view of the publication referred to above.

EXPERIMENTAL

A quartz mercury arc is kept close on the top of a Raman tube cooled by circulating water. Polished aluminum reflectors are used to increase the illumination. A Littrow glass spectrograph with a dispersion of about 10A/mm in the λ4358 region has been used to photograph the scattered spectrum. By using a fine slit (0.03 mm) the Raman spectrum of benzene has been photographed in which the component 984 is clearly revealed. In the same picture 3062 and its companion line 3048 are also recorded very strongly. A set of intensity marks are then put on the same plate by the method of varying slit widths. The lines at 984 and 992 and the lines at 3048 and 3062 along with the intensity marks in the corresponding regions are run through a Moll microphotometer and the relative intensities are deduced in the usual manner with the help of density—log intensity curves.

RESULTS AND DISCUSSION

Figures relating to 992 and its component are not reproduced as they have already been given by a number of earlier investigators. The ratio of intensities of 984 and 992 lines, obtained as the average of three measurements comes out in this investigation as 6 : 100. This is in excellent agreement with the recently reported value of Cheng, Hsueh and Ta-You Wu.[1] No other components are recorded alongside this line.

[1] Cheng, Hsueh and Ta-You Wu, J. Chem. Phys. **6**, 8 (1938).

FIG. 1.

Various investigators [2] have reported results on a study of the components of the 992 cm^{-1} line in benzene. Of these authors Gerlach was the first to suggest that the faint companion at 984 may be due to the principal oscillation of the benzene molecule in which one of the carbon atoms is replaced by its heavier isotope of atomic weight 13. Grassmann and Weiler, Bhagavantam, Specchia and Scandurra and Pattabhiramayya are among those who held that this view was correct. Subsequently Ananthakrishnan expressed the view that the origin of this companion line may not be isotopic. The fact that the recent quantitative study of Cheng, Hsueh and Ta-You Wu already referred to and the author's work reported here both lead to an intensity ratio of 6 : 100 for the companion line in relation to the main line lends strong support to the view that the origin of 984 is isotopic.

The continuous curve in Fig. 1 is a graph showing the intensity distribution in the 3048–3062 lines. The broken lines represent the separate intensities of 3048 and 3062 which together by partial overlapping go to make up the observed intensity curve. These are drawn on the assumption that the lines are symmetrically broadened and it is easily seen that the line at 3062 is very sharp while that at 3048 is broad and diffuse extending on either side to about 25 cm^{-1}. These intensity characters are in perfect agreement with their observed depolarization factors. Veerabhadra Rao[3] and Simons[4] have respectively given 0.88 and 0.89 for the depolarization factor of 3048 and the line should therefore be expected to exhibit a strong wing on either side. On the other hand they have given 0.30 and 0.34, respectively, for the 3062 line and it is accordingly comparatively much sharper. It may easily be seen from the graph that the ratio of the peak intensities of these lines is 1 : 1.35 which agrees with the figures given by Veerabhadra Rao, namely 1 : 1.28. The figures given in this paper are likely to be slightly in error on account of the fact that illumination from the top is adopted and the intensities of two lines whose states of polarization are different are compared.[5] Recent work of Angus and others [6] has shown that both these lines are distinct and they represent two separate fundamental frequencies of the benzene molecule.

The author is highly thankful to Mr. S. Bhagavantam for his kind interest in the work. He is also thankful to the Syndicate of the Andhra University for granting him a research fellowship.

[2] J. Weiler, Zeits. f. Physik **69**, 586 (1931). L. F. Howlett, Can. J. Research **5**, 572 (1931). P. L. Mesnage, J. de phys. **2**, 403 (1931). W. Gerlach, Ber. d. Bayr. Akad. d. Wiss. **1**, 39 (1932). L. and E. Bloch, Comptes rendus **196**, 1787 (1933). P. Grassmann and J. Weiler, Zeits. f. Physik **86**, 321 (1933). O. Specchia and G. Scandurra, Nuovo Cimento **12**, 129 (1935). S. Bhagavantam, Proc. Ind. Acad. Sci. **2A**, 86 (1935). R. Ananthakrishnan, ibid. **3A**, 52 (1936). P. Pattabhiramayya, Thesis submitted to the Andhra University (1937).

[3] Veerabhadra Rao, Zeits. f. Physik **97**, 154 (1935).
[4] Simons, Comm. Soc. Scien. Fenn. **6**, 13 (1932).
[5] A. Veerabhadra Rao, Proc. Ind. Acad. Sci. **7**, (1938).
[6] R. Angus and others, J. Chem. Soc. 912–987 (1936).

Exchange Reactions with Deuterium

II. The Photochemical Exchange Between Deuterium and Hydrogen Chloride

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The exchange reaction between hydrogen chloride and deuterium, initiated photochemically, is found to be a chain reaction with quantum yields ranging from 2 to 19 under the experimental conditions employed. The rate determining step is the reaction $Cl+D_2 \rightarrow DCl+D$. The proportions at the photostationary state are shifted from those at thermal equilibrium in a direction which indicates a somewhat stronger absorption by HCl than by DCl in the region 2000–2150A.

WHEN mixtures of hydrogen chloride and deuterium, or of deuterium chloride and hydrogen, are exposed to light absorbed by the hydrogen chloride or deuterium chloride, an exchange reaction is observed which proceeds rapidly at first, then approaches a photostationary state (Fig. 1) at which the equilibrium proportions are near to, yet definitely different from, the proportions corresponding to thermal equilibrium at the temperature concerned. Using the apparatus previously described,[1] we have studied this exchange with respect to both the initial rate and the photostationary state.

EXPERIMENTAL

The hydrogen chloride-deuterium or deuterium chloride-hydrogen mixtures were exposed, in the quartz reaction vessel R (Fig. 1 of reference 1), to the light of a zinc spark; the effective radiation consisted of the four strong lines in the region 2000–2140A. Quantum yields were obtained by actinometric comparison with the rate of decomposition of ammonia. Measurements of the absorption of hydrogen chloride and ammonia[2] show that for the system used (average light path ~25 mm) absorption of the zinc lines at 2000–2140A may be taken as complete (>95 percent) at ammonia pressures of *ca.* 50 mm or over, while HCl absorbs even more strongly.

The rate of ammonia decomposition was observed through the pressure change, with the assumption that each molecule decomposing produces an increase of one molecule in the gas. The rate of the $HCl-D_2$ exchange was determined through the analysis, using the gas density balance, of the hydrogen-deuterium mixtures obtained. The quantum yield of the exchange reaction (number of H atoms exchanged per quantum absorbed) over any exposure interval is then given by

$$\Phi_{obs}=\frac{2(F_2-F_1)P_{D_2+HD+H_2}\Phi_{NH_3}}{(t_2-t_1)(I_{HCl}/I_{NH_3})(dP_{NH_3}/dt)}, \qquad (1)$$

where F_1, F_2 are the fractions of hydrogen in the hydrogen-deuterium mixture at the beginning and end of the exposure interval, t_1 to t_2 (minutes); $P_{D_2+HD+H_2}$ is the total pressure of the D_2+HD+H_2 mixture; Φ_{NH_3} is the quantum yield of the ammonia decomposition at the pressure used; dP_{NH_3}/dt is the observed rate of pressure increase, in mm/min., when ammonia is

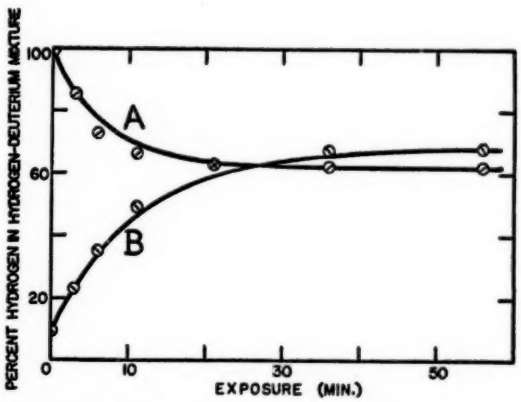

FIG. 1. Hydrogen-deuterium analyses as a function of exposure time. Curve A, for a starting mixture of H_2+DCl, curve B, D_2+HCl.

[1] P. C. Cross and P. A. Leighton, J. Chem. Phys. **4**, 28 (1936).

[2] S. W. Leifson, Astrophys. J. **63**, 73 (1926). H. E. Bacon and A. B. F. Duncan, J. Am. Chem. Soc. **56**, 336 (1934). H. S. Taylor and J. C. Jungers, J. Chem. Phys. **2**, 375 (1934). L. Farkas and P. Harteck, Zeits. f. physik. Chemie **B25**, 257 (1934).

TABLE I.

A. Initial rates in HCl+D_2 mixtures

$P_{D_2+HD+H_2}$ mm	P_{HCl} mm	$\frac{I_{HCl}}{I_{Std}}$	t_2-t_1 min.	F_1	F_2	F_∞	Φ_{obs}	Φ_0
31	79	1	3	0.153	0.270	0.72	1.4	1.9
50	81	1	3	0.153	0.268	0.61	2.2	3.1
53	126	1	3	0.095	0.230	0.68	2.8	3.5
54	330	1	5	0.095	0.295	0.875	2.5	3.2
56	49	1	4	0.095	0.232	0.42	2.2	3.2
62	234	1	5	0.095	0.286	0.775	2.8	3.6
63	176	1	10	0.111	0.432	0.725	2.3	3.7
75	85	0.33	5	0.095	0.198	0.48	5.4	7.0
76	84	0.063	10	0.095	0.200	0.475	14.7	19.0
78	137	0.118	14	0.095	0.275	0.60	9.9	13.5
80	53	1	5	0.095	0.234	0.36	2.6	4.1
113	203	1	5	0.210	0.344	0.64	3.5	5.4
161	82	1	3	0.125	0.203	0.335	4.9	7.0

B. Initial rates in DCl+H_2 mixtures

$P_{D_2+HD+H_2}$ mm	P_{DCl} mm	$\frac{I_{DCl}}{I_{Std}}$	t_2-t_1 min.	F_1	F_2	F_∞	Φ_{obs}	Φ_0
90	175	1	3	1.000	0.853	0.62	5.1	6.5
91	90	1	3	1.000	0.907	0.76	3.3	4.2
175	74	1	3	1.000	0.921	0.85	5.3	7.6

placed in the reaction cell; and I_{HCl}, I_{NH_3} are the incident intensities of 2000–2140A when HCl and NH_3 were in the cell, with complete absorption assumed in both cases.

Since the quantum yield of ammonia decomposition varies with pressure,[3] a standard ammonia pressure of 600 mm was adopted, at which Φ_{NH_3} was taken as 0.18. Runs with ammonia were made at a standard light intensity at which $dP_{NH_3}/dt = 0.31 \pm 0.01$ mm/min.[4] When using HCl−D_2 mixtures, intensities other than this were obtained by varying the distance of the source and assuming the inverse square law. Introducing these modifications, (1) becomes

$$\Phi_{obs} = \frac{1.16(F_2-F_1)P_{D_2+HD+H_2}}{(t_2-t_1)(I_{HCl}/I_{Std})}, \qquad (2)$$

where $1.16 = (2\times 0.18)/0.31$, I_{Std} is the intensity for which $dP_{NH_3}/dt = 0.31$ mm/min. and I_{HCl} is the intensity used in producing the exchange.

As the exposure time is lengthened, or as the photostationary state is approached, Φ_{obs} will decrease, and to obtain the true initial quantum yield it is necessary to extrapolate to zero exposure time and zero exchange. The most satisfactory way of doing this was found to be that based upon the empirical relationship

$$\Phi_t \propto (F_\infty - F_t),$$

which leads to the equation

$$\Phi_0 = \frac{1.16P_{D_2+HD+H_2}I_{Std}(F_\infty-F_0)}{I_{HCl}(1-F_0)(t_2-t_1)} \ln\frac{F_\infty-F_1}{F_\infty-F_2}. \qquad (3)$$

Φ_t, Φ_0 are the quantum yields at the times $t=t$ and $t=0$. F_∞ and F_0 are the fractions of hydrogen in the hydrogen-deuterium mixture at the photostationary state and at the time $t=0$, respectively. The factor $(1-F_0)$ corrects for the hydrogen content of the deuterium at $t=0$. This equation gives satisfactory constants over different time intervals of a given run, and the Φ_0 values agree approximately with those obtained by cumbersome semi-theoretical methods. The extrapolations are from concentration ranges in which the reaction D_2+HCl→HD+DCl predominates over the second-step reaction, HD+HCl→H_2+DCl, and the precision of the results does not warrant any attempt to apply a correction for the effect of the latter. Values of Φ_0 are given in Table I. Since Φ_0 was estimated from the first time interval of each series, F_1 (of Table I) $= F_0$.

Experimental determinations of the amount of exchange at the photostationary state, F_∞, are compared, in Table II, with the value of F for the calculated thermal equilibrium at the temperature of the experiments, 25°C. The photochemical values were obtained by exposing the starting mixtures shown until the analyses became

[3] E. O. Wiig, J. Am. Chem. Soc. **57**, 1559 (1935).
[4] With a cell volume of 150 cc this corresponds to the absorption of 1.4×10^{17} quanta/sec.

TABLE II. *Comparison of photochemical with thermal equilibrium.*

$P_{D_2+HD+H_2}$ MM	$P_{HCl+DCl}$ MM	Initial Analyses		Fraction of H in D_2+HD+H_2 at Equilibrium (25°C)		Ratio $\frac{F_{photochem.}}{F_{thermal}}$
		D_2+HD+H_2	HCl+DCl	Photochemical	Thermal	
53	126	90.5% D	100% HCl	0.68	0.636	1.07
113	203	79.0% D	100% HCl	0.64	0.610	1.05
90	175	100% H	93% DCl	0.62	0.587	1.06

constant; values of the equilibrium constants used in estimating F for the thermal equilibrium were

$$[HD]^2/[H_2][D_2]=3.27,$$
$$[HD][HCl]/[H_2][DCl]=1.27,$$
$$[HD][DCl]/[D_2][HCl]=2.58.$$

Discussion

The initial quantum yields of greater than unity, together with the effect of light intensity (Fig. 2) indicate without question that the exchange is propagated by atomic chains which are stopped by recombinations. Using 102.7 and 101.7 kcal. per mole as the dissociation energies of H_2 and HCl, and taking account of the zero point energies (HCl = 4.2, DCl = 3.0, H_2 = 6.2, HD = 5.4, and D_2 = 4.4 kcal. per mole) one obtains the following energetically favorable reactions for starting mixtures of $HCl+D_2$:

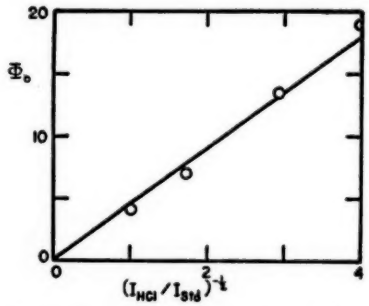

Fig. 2. Quantum yield as a function of light intensity. Solid line is for inverse proportionality between Φ_0 and the square root of incident light intensity. Points are experimental.

$$HCl+h\nu\rightarrow H+Cl, \quad (1)$$
$$H+HCl\rightarrow H_2+Cl+1.0 \text{ kcal.}, \quad (2)$$
$$Cl+D_2\rightarrow DCl+D-1.6 \text{ kcal.}, \quad (3)$$
$$D+HCl\rightarrow HD+Cl+1.8 \text{ kcal.}, \quad (4)$$
$$H+D_2\rightarrow HD+D-1.0 \text{ kcal.}, \quad (5)$$
$$D+HCl\rightarrow DCl+H+1.2 \text{ kcal.}, \quad (6)$$
$$H+H+M\rightarrow H_2+M+102.7 \text{ kcal.}, \quad (7)$$
$$H+D+M\rightarrow HD+M+103.5 \text{ kcal.}, \quad (8)$$
$$D+D+M\rightarrow D_2+M+104.5 \text{ kcal.}, \quad (9)$$
$$H+Cl+M\rightarrow HCl+M+101.7 \text{ kcal.}, \quad (10)$$
$$D+Cl+M\rightarrow DCl+M+102.9 \text{ kcal.}, \quad (11)$$
$$Cl+Cl+M\rightarrow Cl_2+M+56.9 \text{ kcal.}, \quad (12)$$
$$H+Cl_2\rightarrow HCl+Cl+44.8 \text{ kcal.}, \quad (13)$$
$$D+Cl_2\rightarrow DCl+Cl+46.0 \text{ kcal.} \quad (14)$$

For long chain lengths, these reactions give rise to an expression of the following form for the quantum yield:

$$\Phi_0=A+\frac{B[D_2][HCl]([D_2]+\alpha[HCl])}{I^{\frac{1}{2}}M^{\frac{1}{2}}(\sum_{m+n=4}\beta_{mn}[D_2]^m[HCl]^n)^{\frac{1}{2}}}, \quad (4)$$

where A varies between 0 and 2, depending upon the relative velocities of the chain carrying reactions above. B, α, and the β_{mn}'s are also functions of the rate constants of the above reactions. The complicated dependence of Φ_0 upon the concentrations of deuterium and hydrogen chloride as given by Eq. (4) may be approximated by simpler forms in case certain discrepancies in order of magnitude of the chain carrying rate constants prevail, and provided one may assume that all the recombination rate constants are of the same order of magnitude. For example, if $(k_2, k_4, k_6) \gg (k_3, k_5)$, $k_2 \gg (k_4, k_5, k_6) \gg k_3$, $(k_4, k_6) \gg (k_3, k_5) \gg k_2$ or $k_5 \gg (k_2, k_4, k_6) \gg k_3$, $\Phi_0 \propto [D_2]$, whereas if the preceding orders of magnitude are reversed, $\Phi_0 \propto [HCl]$.

From the observation that the quantum yield

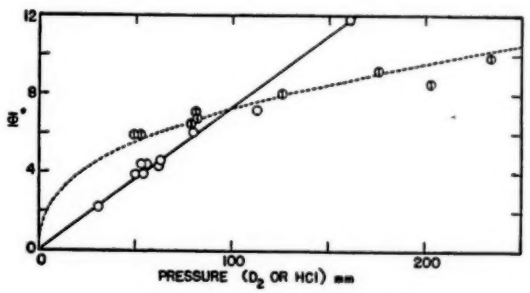

Fig. 3. Quantum yield as a function of the concentration of D_2 and HCl. Solid curve for $\Phi^*=0.073[D_2]$; ○, experimental values of the quantum yield, corrected to the hypothetical conditions of 100 mm total pressure and 100 mm HCl pressure, using $\Phi_0 \propto [HCl]^{0.4}([D_2]+[HCl])^{-0.5}$. Broken curve for $\Phi^*=1.15[HCl]^{0.4}$; ⊙, experimental values corrected to 100 mm total pressure and 100 mm D_2 pressure using $\Phi_0 \propto [D_2]([D_2]+[HCl])^{-0.5}$. Corrections are based upon the empirical formula $\Phi_0^*=0.115[D_2][HCl]^{0.4}$, where Φ_0^* is the quantum yield Φ_0, reduced to the basis of total pressure = 100 mm with the assumption that $M=[D_2]+[HCl]$, i.e., that deuterium and hydrogen chloride are equally effective third bodies for the recombination reactions, and that recombinations at the walls are relatively unimportant.

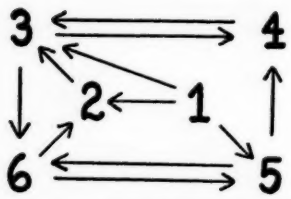

FIG. 4. General scheme for the reaction sequence, showing the various possible chain mechanisms for the exchange. Figures correspond to numbers of the reaction equations (see text).

is pronouncedly more dependent upon the deuterium concentration than upon the hydrogen chloride concentration, as shown in Fig. 3, it is concluded that either (3) is slow compared to (4), or (5) is slow compared to (6), or both; depending upon which of the numerous chains is contributing most to the reaction under the prevailing experimental conditions.

Several investigators have found values near 6.0 kcal. for the activation energy of the reaction $Cl+H_2 \rightarrow HCl+H$.[5] Since this reaction is 1 kcal. endothermic and is the reverse of (2), the activation energy of (2) may be taken as very close to 5.0 kcal. The activation energy of (5) has been reported as 6.5 kcal.,[6] so it is at once indicated that most of the H atoms react by (2), and that chains involving (5) may, with reservations, be excluded from further consideration. The activation energies of the Cl+DH and $Cl+D_2$ exchanges have been estimated to be 0.6 and 1.2–1.4 kcal. higher, respectively, than the activation energy of $Cl+H_2$.[6, 7] These estimates, combined with the zero point energies, give 7.2 kcal. for the activation energy of (3) and 4.6 kcal. for (4).[8] Having as yet no estimate of the activation energy of reaction (6), which competes with reaction (4) for the deuterium atoms, one must admit the possibility of the two chain processes, (2)[(3)(4)]+(3)(4) and (2)(3)(6)+(3)(6)(2), which remain after the elimination of reaction (5) from the general scheme of reaction sequence shown in Fig. 4. Experimentally, reaction (3) is the rate determining step, in keeping with the known activation energies for the first chain process. If (6) were slower than (3), the second chain process would be of negligible importance in the exchange, and the dependence upon $[D_2]$ would still maintain.

For the exchange between DCl and H_2 the chain carrying reactions are

$$DCl+h\nu \rightarrow D+Cl, \quad (1r)$$

$$D+DCl \rightarrow D_2+Cl+1.6 \text{ kcal.}, \quad (2r)$$

$$Cl+H_2 \rightarrow HCl+H-1.0 \text{ kcal.}, \quad (3r)$$

$$H+DCl \rightarrow HD+Cl+0.6 \text{ kcal.}, \quad (4r)$$

$$D+H_2 \rightarrow HD+H+0.8 \text{ kcal.}, \quad (5r)$$

$$H+DCl \rightarrow HCl+D-1.2 \text{ kcal.} \quad (6r)$$

Taking the activation energy of $Cl+D_2$ as 7.2 kcal.,[6] one obtains an activation energy of 5.6 kcal. for (2r). The observed activation energy of (3r) is 6.0 kcal., while the same value is found for (4r) from Cl+DH=6.6 kcal.[6] The activation energy of (5r) has been estimated as 4.8 kcal.[6] In this case the deuterium atoms should react chiefly by (5r) rather than by (2r). The chain carrying steps obtained by eliminating (2r) from the general scheme of reaction sequence analogous to that shown in Fig. 4, and assuming (5r) relatively faster than (3r) become chiefly (5r)(6r), or (5r)[(4r)(3r)]+(3r)(4r), or both, depending upon the relative speeds of (4r) and (6r).

Although our results on initial mixtures of $DCl+H_2$ are unfortunately meager, they definitely indicate a dependence upon the DCl concentration nearly as great as that upon the H_2 concentration, and a quantum yield of the same order of magnitude as for mixtures of HCl and D_2. This can be interpreted as favoring the second chain process given above. For the first chain process to give nearly equal dependence upon $[D_2]$ and [HCl] would require (6r) to have an activation energy near to that of (5r), namely, 4.8 kcal. This would indicate that the exchange between DCl and H_2 should be much faster than that between HCl and D_2, for which the rate determining step has an activation energy of 7.2 kcal. It appears more plausible that the second process, carried by chains of (3r)(4r), both having activation energies of 6.0 kcal., accounted for the observed exchange. Hence (6r) must have an

[5] J. C. Potts and G. K. Rollefson, J. Am. Chem. Soc. **57**, 1027 (1935) give 5.8 kcal., and calculate 5.88 kcal. from the data of Hertel, Zeits. f. physik. Chemie **B15**, 325 (1931). W. H. Rodebush and W. C. Klingelhoefer, J. Am. Chem. Soc. **55**, 130 (1933), give 6.1 kcal.

[6] A. Farkas and L. Farkas, Proc. Roy. Soc. **A152**, 124 (1935).

[7] H. W. Melville, Science Progress, **123**, 499 (1937).

[8] Arbitrarily assuming that the DHCl complex has 0.2 kcal. lower zero point energy than the HDCl complex. (Reference 6.)

activation energy >6 kcal. and (6) >4.8 kcal., indicating that reaction between H (or D) and DCl (or HCl) tends to produce HD and Cl rather than HCl (or DCl) and D (or H).

Of the large number of possible mechanisms for the exchange reaction between HCl and D_2, all of which are of nearly the same order of importance, the results reported here appear to favor chains of reactions (3) and (4) as having the greatest influence on the kinetics of the photochemical exchange under the experimental conditions employed. Similarly, for $DCl+H_2$ mixtures, chains of (3r) and (4r) are indicated. Before these conclusions can be taken as final there are factors which may require further study. These include the effect of wall reactions, the effect of variations in the rates of the chain terminating reactions, the possible difference in the efficiency of HCl and D_2 as third bodies in the atomic recombinations, and the possibility that the activation energies may be in error by an amount sufficient to alter the conclusions drawn from their relative magnitudes. Also, the entire treatment has assumed sufficient diffusion to insure that the local and over-all rates are the same.

At the photostationary state the forward and reverse reactions given above, together with the reactions of the H, D, and Cl atoms with HD molecules, reach a state of balance in which the differences in rates should result in the attainment of thermal equilibrium proportions. Actually the photostationary states are displaced in the direction of higher hydrogen content in the D_2+HD+H_2 mixture than that corresponding to thermal equilibrium (Table II). Although it is uncertain just what significance should be attached to this difference, it probably arises from a stronger absorption by HCl than by DCl in the region 2000–2150A, which is to be expected from the lower zero point energy of DCl. A difference of about 10 percent in the absorption of the zinc lines by HCl and DCl should be sufficient to produce the observed shift of the equilibrium.

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Nonadiabatic Reactions. Chemiluminescence

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It is pointed out that chemiluminescent reactions are necessarily nonadiabatic, since emission of radiation can only occur by transition from an upper to a lower potential energy surface. The restriction imposed by the second law of thermodynamics on the photon yield is,

$$\varphi \leqslant \Delta F/E,$$

where φ is the ratio of quanta evolved to molecules reacted, ΔF is the free energy decrease in the reaction, and E is the energy of the photon emitted. Upper potential energy surfaces are reached either by activation by radiation, which may be that of a black body at the temperature of the reaction, or by the "crossing" of potential energy surfaces. From Audubert's data on the radiation produced by the thermal decomposition of sodium azide approximate surfaces which account for the observations are constructed.

Introduction

THE purpose of the present paper is to treat chemiluminescence as a particular example of the general theory of chemical reactions. A general survey of the field is given along with sufficient examples to illustrate the point of view and the method of treatment.

Chemiluminescent reactions are noteworthy because of the wide variation of the ratio of the number of quanta evolved to the number of molecules reacted. Thus reactions are found experimentally with photon yields ranging from about 0.3 to 10^{-15}. The upper limit of 0.3 for the photon yield is reported for the reaction of sodium

vapor with chlorine, a type of reaction studied by Polanyi and his co-workers.[1] An intermediate value for the yield has been observed by Harris and Parker[2] for the oxidation of 3-aminophthalhydrazide, while reactions with very low photon yields have been studied by Audubert and his associates.[3] Those with the very high photon yields are plainly visible to the unaided eye, while the rather elaborate and sensitive photon counters employed by Audubert and his associates must be employed to detect the radiation emitted by those with very low yields. There is no apparent reason why reactions with photon yields anywhere between zero and one should not be found, subject to the thermodynamic restriction discussed below.

Efficiency of Radiationless Transitions and the Second Law of Thermodynamics

In this section are discussed certain thermodynamic restrictions applying to the efficiency with which normal or excited atoms or molecules can be further excited by ordinary thermal collision processes. Consider a mole of mercury atoms in the metastable 6^3P_0 state dispersed in a foreign gas. Then the energy, E_1 per mole, corresponding to the transition from the excited state, 6^3P_0, to the normal state, 6^1S_0, is almost exactly equal to the free energy difference between the two states. This is true because if the energy of excitation were emitted, the work which it could be made to do would simply be equal to the energy difference between the two levels. Now suppose that a number, N_1, of the excited mercury atoms are raised by thermal collision from the state, 6^3P_0, to the still higher state, 6^3P_1, where their energy referred to the ground state is E_2. In such a process an amount of energy, $N_1(E_2-E_1)/N$, is converted from the thermal energy of the molecules of the inert gas to the free energy of excitation of the mercury. Clearly this increase in free energy for part of the atoms must be balanced by a decrease, at least equal in amount, caused by radiationless transitions from the first excited to the ground state of the mercury atoms. The decrease in free energy, caused by N_2 such transitions, is given by, $N_2(E_1/N)$, and we have the inequality,

$$\frac{N_1(E_2-E_1)}{N} \leqslant \frac{N_2E_1}{N}. \tag{1}$$

Since N_1 plus N_2 equals N, this leads to the relations,

$$\frac{N_1}{N} \leqslant \frac{E_1}{E_2} \quad \text{and} \quad \frac{N_2}{N} \geqslant \frac{(E_2-E_1)}{E_2}. \tag{2}$$

Thus we see that the second law of thermodynamics places an upper limit on the efficiency of excitation by radiationless transitions, and it follows that the number of quanta of energy, E_2/N, that can be emitted is restricted in the same way. In reactions of this kind which do not involve the formation of a new kind of molecule no concentration terms should be included in the free energy expression since normal and excited atoms or molecules cannot be regarded as separate components. If they could be, then energy rich molecules could conceivably be separated from those of low energy by a membrane permeable to only one of the species. Such a membrane, however, would be an example of Maxwell's demon.

The above example is a special case of the more general law,

$$(N_1/N) \leqslant (\Delta F/E), \tag{3}$$

where ΔF is the decrease in free energy in any chemiluminescent reaction, E is the energy per Einstein of the quanta which are emitted, and N_1/N is the photon yield. It may be seen from (3) that in those cases where $\Delta F > E$ these thermodynamic considerations place no restriction on the quantum yield.

The ΔF of Eq. (3) is the decrease in free energy that actually takes place in the reaction vessel; i.e., it includes a term for the free energy of mixing. Thus, even if the equilibrium constant is unity, and consequently the free energy difference of the *pure* products and reactants is

[1] Beutler and Polanyi, Zeits. f. Physik **47**, 379 (1928); Zeits. f. physik. Chemie, **B1**, 3 (1928). Bogdandy and Polanyi, Zeits. f. physik. Chemie **B1**, 3 (1928). Polanyi and Schay, ibid. **B1**, 30 (1928).

[2] Louis Harris and Almon S. Parker, J. Am. Chem. Soc. **57**, 1939 (1935).

[3] See, for example, R. Audubert, J. Chim. Phys. **33**, 507 (1936).

zero, there is still a free energy decrease in the reaction due to the mixing of reactants and products. As an example let us consider the problem of how much radiation can be evolved if a mole of A reacts to form $\frac{1}{2}$ mole of its optical isomer, B, in ideal solution with A. Here the equilibrium constant is certainly unity and the free energy change is due entirely to the entropy of mixing. This is equal to R ln 2, which corresponds to a free energy decrease of 0.415 kcal. at 300°K. The maximum photon yield from such a reaction is found by application of Eq. (3) to be about 1 percent for a wave-length of 6900A and correspondingly different for other wave-lengths. Since actual reactions in general have much larger free energy decreases, as well as photon yields much below this value, it is obvious that the restriction imposed by Eq. (3) will rarely, if ever, be the factor limiting the yield. When pure A first forms B the free energy decrease per molecule is extremely large so that initially there is no thermodynamic restriction on the quantum yield. As the concentration of B approaches equality with that of A the thermodynamically allowed φ drops to zero. Our definition has been couched in terms of the overall ΔF and φ.

The question has sometimes been asked whether or not it is possible for an endothermal reaction to be chemiluminescent. The answer given here is that if the reaction is spontaneous, i.e., if it involves a free energy decrease, then it can be chemiluminescent with a maximum photon yield given by Eq. (3). How nearly this maximum efficiency is approached is purely a question of mechanism and can only be solved by reaction rate theory.

Activation by Black-Body Radiation

Since chemiluminescent reactions must necessarily involve the transition of molecules from upper to lower potential energy surfaces, the theory of these reactions must provide some mechanism for reaching an upper level. One such possible mechanism is activation by means of absorption of black-body radiation originally proposed by Perrin and W. C. McC. Lewis as the mechanism for the activation of molecules

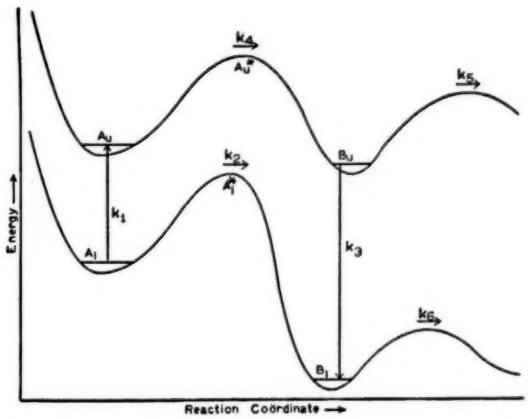

FIG. 1. Schematic energy diagram on which a chemiluminescent reaction could take place by means of activation by black-body radiation.

undergoing ordinary chemical reactions. There is abundant evidence showing that the reaction rates via this mechanism are ordinarily slower by a factor of about 10^5 than the rates resulting from activation by thermal collision when the activation energies are the same. However, activation by black-body radiation may be of importance in chemiluminescent reactions.

Figure 1 illustrates a potential energy surface on which it would be possible for a chemiluminescent reaction to take place by means of the black-body mechanism of activation.

Here A_l (lower) and A_u (upper) refer to the species that are reacting in the normal and excited states respectively; B_l and B_u have the same significance for the products of reaction. A_l^* and A_u^* indicate the activated molecules for the lower and upper surfaces respectively. When enclosed in parentheses, these symbols refer to concentrations. The k's indicate the specific reaction rate constant for a process proceeding in the direction indicated by the arrow. When the reaction rate constants refer to directions opposite to that indicated by the arrow, they will be primed.

At equilibrium between A_u and A_l, the rates in the two directions will be the same and a discussion applying to k_1' will be applicable to k_1. An expression for k_1' can be written in terms of the Einstein coefficient for spontaneous transition, $\mathbf{A}_{ul}$, from the upper state corresponding to

A_u, to the lower state, A_l. We have[4]

$$k_1' = \sum_u \sum_l \left\{ \omega_u \frac{\mathbf{A}_{ul}}{1-\exp(-h\nu_{ul}/kT)} \times \exp(-\epsilon_u/kT) \right\} \{\sum_u \omega_u \exp(-\epsilon_u/kT)\}^{-1}. \quad (4)$$

Here ω_u is the usual statistical weight, ν_{ul} is the frequency of the emitted radiation, and ϵ_u is the energy in the excited state referred for convenience to the lowest state of the normal molecule, A_l. If the radiation density is equal to that of a black body at the temperature of the reaction, the states u and l will be in equilibrium and we have the relation,

Equilibrium constant

$$= \frac{k_1'}{k_1} = \frac{\sum_l \omega_l \exp(-\epsilon_l/kT)}{\sum_u \omega_u \exp(-\epsilon_u/kT)}. \quad (5)$$

Equations (4) and (5) may be combined to give an expression for k_1.

$$k_1 = \sum_u \sum_l \left\{ \omega_u \frac{\mathbf{A}_{ul}}{1-\exp(h\nu_{ul}/kT)} \exp(-\epsilon_u/kT) \right\} \times \{\sum_l \omega_l \exp(-\epsilon_l/kT)\}^{-1}. \quad (6)$$

The expressions for k_4' and k_4 are identical with those for k_1' and k_1 except that in this case the summations are made over the energy levels of B_u and B_l, respectively.

Since expressions (4) and (6) represent the total transition probability between states we expect that a satisfactory approximate expression can be secured by taking a transition probability averaged over all states, and an averaged energy of activation secured in the same way. This gives for the rate expression,

$$k_1 = (1/\tau) \exp(-E/kT). \quad (7)$$

Here $1/\tau$ and E are interpreted as being the reciprocal mean lifetime and energy difference between the two states, respectively, and the difference in entropy between the upper and lower states has been neglected. When sufficient information is available the exact expression (6) will be used. For many atomic transitions, $1/\tau$ is of the order of 10^8 and is probably not greatly different for transitions in molecules. For forbidden transitions it may drop to values as small as 10^{-2}.[5]

We now go on to develop a general theory of chemiluminescent reactions involving as one step the transition from a lower to an upper level by means of black-body radiation. This can be done conveniently by referring to the schematic energy diagram in Fig. 1. When there is not too much difference between the free energy of the activated complex, A_u^* on the upper surface and A_l^* on the lower surface, an appreciable fraction of the reaction will proceed by way of the upper surface and will therefore emit radiation in the transition, $B_u \rightarrow B_l$. At equilibrium this will just be balanced by the absorption $B_l \rightarrow B_u$, but in a system containing more than the equilibrium amount of reactant, A_l, more energy of this wave-length will in general be emitted than absorbed.

As an example we set up the rate and photon yield expressions for the particular case where all the reactions are first order with respect to the substances indicated in Fig. 1. Any dependence on other substances is implicitly included in the k's. We can write in the usual way.

$$d(A_u)/dt = k_1(A_l) + k_4'(B_u) - (A_u)(k_1' + k_4) = 0, \quad (8)$$

$$d(B_u)/dt = k_4(A_u) - (B_u)(k_4' + k_5 + k_3) = 0. \quad (9)$$

Here the processes with specific rate constants, k_3' and k_5' have been neglected. Combining Eqs. (8) and (9) so as to eliminate (A_u) we have,

$$(B_u) = \frac{k_4 k_1 (A_l)}{(k_1' + k_4)(k_4' + k_5 + k_3) - k_4 k_4'}. \quad (10)$$

Then if dN/dt is the rate of emission of light we have,

$$\frac{dN}{dt} = \frac{k_3 k_4 k_1 (A_l)}{(k_1' + k_4)(k_4' + k_5 + k_3) - k_4 k_4'} \quad (11)$$

[4] See for example, Condon and Shortley, *The Theory of Atomic Spectra*, (Cambridge Press, 1935), Chap. IV, or Tolman, *Statistical Mechanics with Applications to Physics and Chemistry* (Chemical Catalog Co., 1927), Chaps. 16 and 21.

[5] Condon and Shortley, reference 4, p. 282.

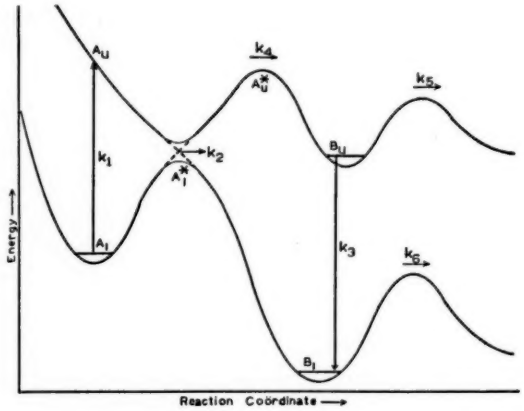

FIG. 2. Schematic energy diagram illustrating the "crossing" mechanism of activation. The separation of the two surfaces at the point corresponding to A_l^* is exaggerated.

and for the photon yield, φ, we obtain,

$$=\frac{(dN/dt)}{-d(A_l)/dt}$$

$$=\frac{k_3}{k_3+k_5+\dfrac{k_2[(k_1'+k_4)(k_4'+k_5+k_3)-k_4k_4']}{k_1k_4}} \quad (12)$$

if we note that $d(A_l)/dt$ is given by

$$-d(A_l)/dt=dN/dt+k_5(B_u)+k_2(A_l). \quad (13)$$

We will consider three limiting cases for the rate dN/dt, in each case neglecting the quenching process involving k_5.

Case I.—When the rate determining step is the transition $A_l \rightarrow A_u$ then $k_1' \ll k_4$ and

$$\varphi=k_1/(k_1+k_2). \quad (14)$$

Case II.—When the rate determining step is the transformation $A_u \rightarrow B_u$ then $k_4 \ll k_1'$, $k_4' \ll k_3$ and,

$$\varphi=\frac{k_4(k_1/k_1')}{k_4(k_1/k_1')+k_2}. \quad (15)$$

Case III.—Finally, when the rate determining step is the transition $B_u \rightarrow B_l$ then $k_3 \ll k_4'$ and

$$\varphi=\frac{k_3(k_1k_4/k_1'k_4')}{k_3(k_1k_4/k_1'k_4')+k_2}. \quad (16)$$

The quantities in parentheses in Eqs. (15) and (16) are equilibrium constants between upper and lower levels.

From Fig. 1 it may be seen that a photon yield approaching the thermodynamically allowable maximum given by Eq. (3) is not to be expected unless the upper surface at the point marked A_u^* approaches close to the lower surface. For higher temperatures where the rate corresponding to k_1 is the slow step, a high yield will be obtained if the energy difference between A_u and A_l is very small.

ACTIVATION WITHOUT BLACK-BODY RADIATION

In this case chemiluminescence will arise because of the nonadiabatic "crossing" of energy levels. This is illustrated in the schematic diagram (Fig. 2).

The essential difference between Figs. 1 and 2 is that in the latter case the two potential surfaces come very close together and to a first approximation they may be said to cross making possible a nonadiabatic jump of the system from the lower to the upper surface without absorbing radiation. The approximate expression for the probability of this process happening has been given by Zener[6] and by Landau[7] and the expression has been applied in a treatment of the nonadiabatic decomposition of N_2O.[8] This expression is

$$P=\exp\left\{\frac{-4\pi^2\epsilon_{12}^2}{hV|s_1-s_2|}\right\}. \quad (17)$$

Here $|s_1-s_2|$ is the absolute difference in slope between the two dotted lines in Fig. 2 while $2\epsilon_{12}$ is the difference in energy between the upper and lower surfaces at the activated point corresponding to the species, A_l^*. V is the velocity along the reaction coordinate at this point.

The transmission coefficient,[9] κ, may be related to P in the following way. If, of the number of molecules that reach the activated point corresponding to A_l^*, a fraction P jump to the upper surface, then $1-P$ will be the fraction that remains on the lower surface. Those on the

[6] C. Zener, Proc. Roy. Soc. **A137**, 696, (1932); **A140**, 660 (1933).
[7] Landau, Physik. Zeits. Sowjetunion **2**, 46 (1932).
[8] A. E. Stearn and H. Eyring, J. Chem. Phys. **3**, 778 (1935).
[9] H. Eyring, J. Chem. Phys. **3**, 107 (1935).

upper surface may return to the lower surface in two ways, one corresponding to reaction and the other corresponding to a return to the initial configuration, A_l. κ, the probability that the system will react after having once reached the activated configuration, is given by,

$$=1-P+P^2[(1-P)+(1-P)^3$$
$$+(1-P)^5+\cdots]=2(1-P)/2-P, \quad (18)$$

which reduces to $2-2P$ when P is almost equal to unity. Further, when this is the case, the exponential in Eq. (17) may be expanded and the higher powers of $(4\pi^2\epsilon_{12}^2)/(hV|s_1-s_2|)$ dropped so that we have as an approximate expression for κ,

$$\kappa=(8\pi^2\epsilon_{12}^2)/(hV|s_1-s_2|), \quad (19)$$

which is valid for values of P that are not too far from unity.

One other possible mechanism for reaching the upper surface is that corresponding to the transition with the specific rate constant, k_1. This will in general, however, not be of importance for the case of activation by black-body radiation unless the upper surface comes very close to the lower one at a point directly above the one corresponding to A_l on the lower surface. However, if activation is brought about by illuminating the system with radiation of the proper wave-length this mechanism for reaching the upper surface may become the important one. This would be a case of photoreaction which might be accompanied by fluorescence. The general considerations discussed above also apply in this case.

Considering now the rate determining step for the luminescent reaction we see that it can be either the process with specific rate constant, k_4, or the one with specific rate constant, k_3. When the mean life of B_u is of the order of 10^{-8} sec., then the rate corresponding to k_4 will be the slow step if the energy of activation for k_4' is less than about $23T$ cal. or 6900 cal. at room temperature. For energies of activation greater than $23T$ cal., k_3 will become the slow process. These approximate computations neglect any difference in entropy between B_u and A_u^*.

There is, however, an important group of reactions which involve the possibility of emitting radiation, but where the mean life of the excited molecules may be of the order of minutes. This is the case for those instances where the "crossing" of potential energy surfaces is due to a change in multiplicity. The general expression for the Einstein transition probability $\mathbf{A}(a, b)$ between level a and b can be written as the sum of three terms, i.e., one for the electric dipole, one for the magnetic dipole and one for the quadrupole radiation, respectively. The transition probability can be written in the form:[10]

$$\mathbf{A}(a, b)=(64\pi^4\sigma^3/3h)[|(a|\mathbf{P}|b)|^2$$
$$+|(a|\mathbf{M}|b)|^2+(3/10)\pi^2\sigma^2|(a|\mathbf{N}|b)|^2].$$

Here σ is the wave number of the emitted radiation;

$$\mathbf{P}=-e\sum_i \mathbf{r}_i; \quad \mathbf{M}=-(e/2\mu c_i)\sum_i(\mathbf{L}_i+2\mathbf{S}_i);$$
$$\mathbf{N}=-e\sum_i \mathbf{r}_i\mathbf{r}_i;$$

where e is the charge on the ith electron whose vector distance is $\mathbf{r}_i$; μ is the mass of the electron; $\mathbf{L}_i$ the orbital angular momentum, and $\mathbf{S}_i$ the spin angular momentum. For forbidden lines $|(a|\mathbf{P}|b)|$ equals zero due to a change in multiplicity and $\mathbf{A}(a, b)$ instead of being about 10^8 is much smaller. For example the interpretation of the nebular lines of *OIII* as given by Condon[11] leads to an Einstein transition probability of $\mathbf{A}=0.018$ sec.$^{-1}$ for the $D_2\rightarrow 3P_2$ transition and an $\mathbf{A}=0.006$ for the transition $D_2\rightarrow 3P_1$. The transition probabilities for quadrupole radiation are found to be about 1000 times smaller. For transitions involving a change in multiplicity the magnetic dipole transition probabilities are known to be proportional to $(\epsilon_{12}/(E_1-E_2))^2$ where ϵ_{12} is the spin orbital interaction between the upper and lower state and E_1-E_2 is the energy emitted in the transition. Now this ϵ_{12} is formally the same as the ϵ_{12} occurring as a factor in the transmission coefficient for k_2 discussed above. The difference in the two ϵ_{12}'s is that they are the spin orbital interactions calculated for different configurations but an examination of multiplet widths (which enables one to calculate ϵ_{12} for atoms)[12] indicates that the value for ϵ_{12}

[10] Condon and Shortley, reference 4, p. 90 etc.
[11] Condon, Astrophys. J. **79**, 217 (1934). Condon and Shortley, reference 4, p. 282.
[12] See Condon and Shortley, reference 4, p. 268.

often changes only slightly when an atom becomes a part of a diatomic hydride molecule. There are notable exceptions to this rule among nonhydride molecules.[13] Thus for forbidden magnetic dipole transitions of $B_u \rightarrow B_l$ we expect $(\kappa_2(kT/h))$ often to be proportional to $1/\tau_3$, the former being about 10^{10} times the latter. Thus if k_3 is to be of the same order as k_2 we must then have $(E_1-E_2)/RT \approx 10^{10}$; or $E_1-E_2 \approx 46T$ cal., i.e., if the reactions are to proceed at about the same rate at room temperature then the energy of B_u should be about 14 kcal. lower than A_l*. From this one sees that there are types of "crossing" potential surfaces which can lead to high photon yields even when the emission process involves a change of multiplicity and is consequently forbidden in the electric dipole approximation. For "crossing" potential surfaces which, however, do not involve forbidden transitions for $B_u \rightarrow B_l(\kappa_2(kT/h))$ will probably be more nearly 10^5 than 10^{10} times $1/\tau_3$. This case has already been discussed.

The quenching of radiation can in general be expected to proceed by reaction over the potential hills marked k_5 in Figs. 1 and 2. If this is the case the amount of quenching for a given activation energy can be expected to be proportional to the mean life of B_u. Quenching can thus be expected to be a much more important factor for cases involving forbidden transitions than for other instances where the mean lifetimes are very short.

In Fig. 2 a particular manner of "crossing" of the two surfaces is shown. Clearly the photon yield for radiation will be higher the higher the activation energy hill for the nonluminescent reaction is in comparison to the luminescent one. If, instead of "crossing" before the system reaches the activation hill, A_l*, the "crossing" occurs afterwards, the chemiluminescent efficiency should approach the thermodynamic maximum. In this case there would be no difference in activation energy for the luminescent and nonluminescent reactions, and the entire difference in rate would arise from the difference in the transmission coefficients for the two alternative processes.

It is of some interest to note that the thermodynamic considerations discussed in Section II place a lower limit on the transmission coefficient corresponding to the reaction rate constant, k_2 of Fig. 2. Thus, κ cannot become so small that the condition imposed by Eq. (3) will be violated.

[13] See R. S. Mulliken, Rev. Mod. Phys. **4**, 37 (1932).

Chemiluminescent Reactions of Metallic Azides

As an example of the interpretation of data that may be obtained, we consider a series of chemiluminescent reactions studied by Audubert,[14] the decomposition of metallic azides. It appears likely that the potential energy surface for these reactions is similar to that given in Fig. 1, although a surface of the type illustrated by Fig. 2 is not entirely precluded. However, evidence will be presented tending to show that if the luminescent reaction proceeds by way of "crossing" of potential energy surfaces, the crossing cannot be due to a change of multiplicity.

Audubert finds that the azides of silver, lead, sodium and potassium all emit radiation lying in the neighborhood of 2000A, about 140 kcal. per mole. This we interpret as corresponding to the transition, B_u to B_l of Figs. 1 or 2, and the fact that all the different azides emit light of about the same frequency seems to indicate that the same molecule is radiating in all cases.

The decomposition of NaN_3 furnishes an example of what might be expected to be a fairly common phenomenon, a chemiluminescent reaction in which the activation energy for photon emission show two quite different values. The rate determining step at low temperatures is due to the reaction, $A_l \rightarrow B_u$, proceeding with an activation energy of about 48 kcal. The activation energy of 23 kcal. given in column four of Table I may be either that for the reaction of B_u going to B_l shown in Figs. 1 or 2 or that for the transition, A_l to A_u, of Fig. 1. However, the following consideration will throw some light on the question. If the mechanism for the reaction is that illustrated by Fig. 2, then the "crossing" of the two surfaces cannot be due to change of multiplicity. For transitions involving change of multiplicity the value of τ in Eq. (7) is greater by a factor of about 10^{10} than for other transitions which are not forbidden. But the temperature at which the two rates corresponding

[14] Audubert, J. Chem. Physique **34**, 29 (1937).

to the two activation energies become equal is the point at which the two straight lines obtained by plotting ln k against $1/T$ intersect. By referring to Fig. 3 of Audubert's paper this temperature is found to be 640°K for the case of NaN_3. We can then set up the equation,

$$\frac{kT}{h}\exp\left(\frac{-48\pm2\text{ kcal.}}{RT}\right)=\frac{1}{\tau}\exp\left(\frac{-23\pm2\text{ kcal.}}{RT}\right)$$

and solve for τ. For this case we get values for τ of approximately 3×10^{-10} and 10^{-13} sec. for upper and lower limits, respectively. These values are even smaller than the value of about 10^{-8} sec. that would be expected for most allowed transitions, and are *very* much smaller than would be expected for transitions involving change of multiplicity. We accordingly draw the conclusion that if the potential energy surface for the decomposition of the azides is similar to that illustrated in Fig. 2, the "crossing" does not involve a change in multiplicity.

It is not possible to decide from the evidence at hand whether the process with the activation energy of 23 kcal. corresponds to the reaction of B_u going to B_l of Figs. 1 and 2 or to the reaction of A_l going to A_u of Fig. 1. This point could, however, be decided experimentally by increasing the density of radiation at the wave-length corresponding to 23 kcal., about 12,000A. This would speed up the transition A_l to A_u, but would alter the velocity of B_u going to B_l by only a negligible amount.

In confirmation of our suggestion that the decomposition reactions of the azides all proceed by the same mechanism, it will be noted that the activation energies for the reaction A_l going to B_u are the same for the three cases recorded in Table I. Likewise the activation energies for the other step in the luminescent reaction are essentially the same for the two cases recorded. It appears probable that if the decomposition reaction of $Pb(N_3)_2$ could be followed to a low enough temperature an activation energy for the reaction of A_l going to B_u would be found. Conversely, if the decomposition reactions of AgN_3 and KN_3 could be studied at high enough temperatures another activation energy should be found with the value of about 25 kcal.

TABLE I.

Substance	Heat of Reaction[15a]	Energies of Activation for the Reactions, (See Fig. 1 or 2)		
		k_2 $A_l\rightarrow B_l$[15b]	k_1 $A_l\rightarrow A_u$[15c] or k_3 $B_u\rightarrow B_l$	k_4 $A_l\rightarrow B_u$[15c]
AgN_3	− 67.3 kcal.			47±1 kcal.
$Pb(N_3)_2$	−103.0	38 kcal.	25±1 kcal.	
NaN_3	− 5.0(?)	34.4	23±2	48±2
KN_3	− 0.5(?)	36.1		48±2

[15a] Data quoted by Audubert. For AgN_3 and $Pb(N_3)_2$ the reference to the original work is, Wöhler and Martin, Zeits. ges. Schiess Sprengstoffen, 12, 1 (1918). For the alkali azides Audubert gives no reference and we have been unable to find one.
[15b] Garner and Mark, J. Chem. Soc. 657 (1936).
[15c] Audubert apparently omitted the factor of 2.3 in calculating his activation energies from the slope of the curves in which $\log_{10} k$ is plotted against $1/T$.

We now attempt to construct as complete a potential energy surface for the decomposition of NaN_3 as is possible by using the data at hand. A possible surface that accounts for most of the facts is shown in Fig. 3.

The amount of free energy, 26±2 kcal./mole, by which the maximum of the upper curve lies above the maximum point of the lower one is obtained from Audubert's value of the photon yield. He states that the order of magnitude of this quantity is 10^{-9} to 10^{-10} for the azides which leads to the equation:

$$\exp-(\Delta F_4\ddagger-\Delta F_2\ddagger)/RT=10^{-9}\text{ to }10^{-10},$$

$$\Delta F_4\ddagger=\Delta F_2\ddagger+26\pm2\text{ kcal./mole.}$$

To the approximation to which we can neglect $T(\Delta S_4\ddagger-\Delta S_2\ddagger)$ this is also the difference in energy of activation for the two reactions.

The difference in energy between the A_l* and A_u* can be obtained by a second method. This energy difference is found to be $(48\pm2)-34=14\pm2$ kcal./mole from the temperature coefficient of the photon yield. The disagreement indicates either that the value of about 10^{-9} for the photon yield is too low, or that it is not a good approximation to neglect the difference in entropy between the activated complexes on the lower and upper surfaces.

The emission of radiation of a frequency corresponding to an energy of 140 kcal. per Einstein presents an interesting problem. The energy difference between A_l and B_u according to the data cannot be greater than about 23 kcal., and may be less than this depending on whether the

transition A_l to A_u or B_u to B_l is the slow process. Audubert quotes the figure 5 kcal./mole for the heat emitted during the decomposition of NaN_3 into solid sodium and gaseous nitrogen. If this figure is correct and if there is no energy difference between the stable final product and the product obtained immediately after emission of the photon, then 23 molecules of NaN_3 would each have to contribute their energy of reaction in order to build up an excited molecule capable of emitting a photon of the required energy. On the other hand, this difficulty is not encountered in the case of AgN_3 and $Pb(N_3)_2$. In these cases it is only necessary to assume that two azide groups are involved in the steps leading to the emission of each photon in order to have sufficient energy available.

Since all the reactions proceed with about the same quantum yield it does not appear to be probable that the luminescent reaction for the azides of silver and lead involve only two azide radicals per quantum emitted while the same reaction for the azides of the alkali metals involves twenty molecules or more. What appears to us to be more probable is that the quoted values for the heats of decomposition of the alkali azides are incorrect.

The work of Sklar[15] on the theory of color of organic compounds makes it possible to offer a tentative suggestion concerning a possible structure of the excited molecule that emits the quanta of wave-length 2000A. Sklar expresses the energy levels corresponding to the absorption of light of different frequencies in terms of the resonance energy of the benzene molecule. He finds the first strong absorption band to be at a wave-length of about 2000A, just the same wave-length as the light that is emitted during the decomposition of the azides. This fact, along with the observation that in the case of the azides of lead and silver the energy of two azide radicals is necessary to furnish the energy emitted in one photon, leads us to suggest that a cyclic nitrogen compound with six nitrogen atoms arranged in a ring may be the molecule emitting the radiation. Although the total energy difference between cyclic N_6 and $3N_2$ must be very much less than that between C_6H_6 and $3C_2H_2$, it is not unreasonable to assume that the resonance energy of the cyclic N_6 would be about the same as that of benzene. If this were the case the absorption bands according to Sklar's theory would be expected to be about the same.

[15] Alfred L. Sklar, J. Chem. Phys. **5**, 669 (1937).

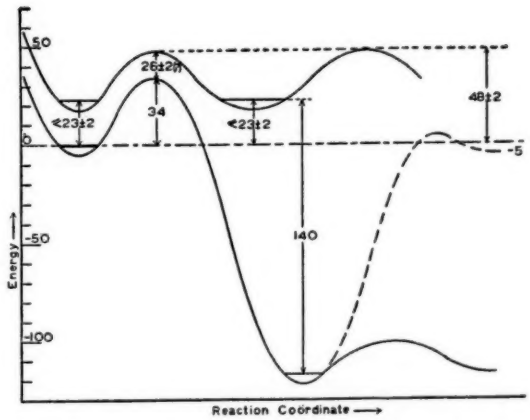

FIG. 3. Schematic energy diagram for the chemiluminescent decomposition of sodium azide. The energy units are kcal./mole. A surface similar to Fig. 2 is not completely excluded.

It should be pointed out that the energy of the reacting system immediately after emitting a photon is not necessarily greater than the energy of the final products. This, of course, is not true of the free energy which must be lower for the stable products than for any intermediates. In this connection it may be pointed out that if the value of 5 kcal. for the heat of decomposition of NaN_3 is accepted and if the cyclic N_6 molecule is the immediate product after the radiation is emitted, then the N_6 molecule would be expected to be thermodynamically stable up to about 1300°K. This estimate is based on the assumption that the difference between the entropy of N_6 and $3N_2$ is about the same as the difference in entropy between C_6H_6 and C_2H_2. Even if the reaction mechanism is quite different from that proposed here, an energy difference of the order of magnitude of that shown by the dotted curve of Fig. 3 seems to be entirely unreasonable.

CONCLUSION

Although quenching processes play an important role in most reactions involving radiation, they have been only briefly mentioned above. There are many data available on the quenching of excited atoms in the gas phase by collision with foreign atoms or molecules. These

data have generally been interpreted in terms of an effective cross-sectional area, but a more rational explanation is to be found in the "crossing" of potential energy surfaces. For many simple cases the surfaces could be constructed for direct comparison with experiment, and work along these lines is planned. Aside from these cases, there are quantitative data on quenching for only a few cases. Anderson[16] has obtained data on the effect of dissolved salts on the chemiluminescence of cypridine luciferin, and has found increases in the photon yield in some cases. This result is understandable either as a change in the activity coefficients of the reactants or activated complexes for some of the reactions or as a change in the important mechanisms. One possible example of the latter type would be the removal of a quenching agent originally present.

The phenomenon of mitogenetic ray emission has been very extensively studied with rather contradictory results, and a review has been written by Hollaender and Claus.[17] Although we do not attempt to express an opinion regarding the physiological effects of such radiation, the occurrence of many weak chemiluminescent reactions in living organisms is to be expected in the light of the mechanism for their occurrence discussed above.

Audubert and Victorin[18] have investigated the ultraviolet luminescence occurring at aluminium anodes showing an electric valve effect. While it is difficult to assign the precise mechanism from the available experimental material it apparently is possible to understand these results in terms of "crossing" potential surfaces.

The following general considerations regarding chemiluminescence in flames may be mentioned. Figs. 1 and 2 show only a single upper potential energy surface. For complicated molecules there will be many such surfaces and if the activated complex on any such surface is denoted by $A_u^*(n)$, the concentration of $A_u^*(n)$ is determined by the temperature and by the free energy difference between A_l and $A_u^*(n)$ and for sufficiently high temperatures many of these upper levels will contribute chemiluminescent reactions. On the other hand the frequency of the emitted light is determined by the energy difference between $B_u(n)$ and B_l. Here $A_u^*(n)$ and $B_u(n)$ are denoted by simply A_u^* and B_u on the lowest excited surface represented in Figs. 1 and 2. Since reactions proceed with a free energy decrease, the free energy of B_l will be lower than that of A_l. We thus expect that in general the energy of the light emitted will be greater than the free energy of activation of A_l going to $A_u^*(n)$, but that the amount of radiation of the corresponding frequency will, in the absence of quenching processes, be governed by the energy of activation. Quenching processes may, however, destroy any correspondence of this kind, especially if the excited molecule, $B_u(n)$, has a long mean life. The black-body spectrum corresponding to the temperature of the flame will, of course, form a background on which is superimposed the radiation from chemical reactions.

In a recent paper dealing with the interpretation of alkali halide-thallium phosphors, Dr. Frederick Seitz[19] has concluded that it is possible for a particular phosphor containing an excited electron to pass less readily over a potential barrier by an adiabatic process than it does over a higher barrier which can only be reached by absorption of radiation. This case, if correctly interpreted, is of great interest in providing the only known type of reaction in which the rate by the radiation mechanism is actually faster than the rate resulting from a collision mechanism involving a lower energy of activation.

We want to thank Doctor Rubert S. Anderson, Professor M. Polanyi and Professor Hugh S. Taylor for helpful discussions while this work was in progress. One of us (H.E.) is glad to have this opportunity of expressing his appreciation to the Rockefeller Foundation for the opportunity of working in England.

[16] R. S. Anderson, J. Am. Chem. Soc. **59**, 2115 (1937).
[17] A. Hollaender and W. D. Claus, J. Opt. Soc. Am. **25**, 270 (1935).
[18] Audubert and Victorin, J. Chim. Phys. **34**, 18 (1937).
[19] F. Seitz, J. Chem. Phys. **6**, 150 (1938).

The Decomposition of Mercury Dimethyl

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The thermal and photochemical decompositions of mercury dimethyl have been studied in presence and absence of hydrogen. The thermal process occurs measurably above 290° in absence of hydrogen and is complex, yielding ethane, methane and carbonaceous products. In presence of hydrogen there is no carbonaceous deposit and methane is predominantly formed with consumption of hydrogen, which accelerates the decomposition. The influence of surface effects has been noted. The photo-decomposition has been studied from 50–300°C. In absence of hydrogen, ethane is practically exclusively formed up to 200°. In presence of hydrogen, methane is formed at all temperatures, in increasing amounts with increase of temperature. A mechanism based on photo-decomposition to free methyl radicals with association to yield ethane and reaction with hydrogen to yield methane has been quantitatively determined. For the activation energy $CH_3+H_2=CH_4+H$ a value of 9 ± 2 kcal. has been deduced.

THE reaction $CH_3+H_2\rightarrow CH_4+H$ has recently been shown to be of importance as an intermediate process in exchange reactions involving the simpler saturated hydrocarbons,[1, 2] and any independently derived information regarding its energetics would be of value in explaining the results obtained. The present investigation was undertaken in an attempt to provide such information, the metal alkyl, mercury dimethyl, being used as a source of free methyl radicals. It was first necessary to establish the conditions under which the decomposition of mercury dimethyl proceeded at a measurable rate: then, from the effect of added hydrogen upon the kinetics of the decomposition, some conclusions were drawn regarding the process under consideration.

Direct evidence of the momentary existence of free organic radicals in the decomposition of metal alkyls was first obtained by Paneth and Hofeditz,[3] who passed lead tetramethyl vapor through a quartz tube heated at one point to about 700°, and detected free methyl radicals by causing them to combine with a number of metals deposited as mirrors in the cool parts of the tube. It was found[4] that free ethyl could be prepared from lead tetraethyl and identified in a similar manner, but the higher analogues were apparently unstable at the temperatures necessary for the decomposition of the corresponding metal alkyls. Indirect evidence of the thermal liberation of free radicals from mercury dimethyl has been furnished by Taylor and Jones[5] who showed that such postulated radicals induced the polymerization of ethylene at reaction temperatures of 200–300°. Frey[6] also observed that the addition of 1 percent of the compound to butane brought about the decomposition of twenty equivalents at 525°, at which temperature the hydrocarbon itself would not have been affected in the time of the experiment; this result can only be explained as due to chain initiation by free methyl radicals. Rice, Rodowskas and Lewis[7] obtained similar results with acetone containing 1 percent of mercury dimethyl in the temperature range 350–400°: the relatively short chains observed were attributed to more effective chain-breaking processes than in the case of butane.

The photochemical decomposition of mercury dimethyl has been somewhat more extensively investigated, notably by Terenin and coworkers.[8] The absorption spectrum shows a continuum beginning at 2800A and extending further into the ultraviolet, upon which is superimposed a group of diffuse bands in the

[1] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937).
[2] Morikawa, Benedict and Taylor, J. Chem. Phys. **5**, 212 (1937).
[3] Paneth and Hofeditz, Ber. **62**, 1335 (1929).
[4] Paneth and Lautsch, Ber. **64**, 2702 (1931).
[5] Taylor and Jones, J. Am. Chem. Soc. **52**, 1111 (1930).
[6] Frey, Ind. Eng. Chem. **26**, 200 (1934).
[7] Rice, Rodowskas and Lewis, J. Am. Chem. Soc. **56**, 2497 (1934).
[8] Terenin, J. Chem. Phys. **2**, 441 (1934); Acta Physicochim. U. S. S. R. **1**, 762 (1935); Terenin and Prileshajeva, Trans. Faraday Soc. **31**, 1483 (1935).

region 2100–1970A. Terenin postulated a mechanism of decomposition involving free methyl radicals, and reported their identification by the metal mirror technique, the maximum concentration of radicals being observed when light in the 2100A region was used. Linnett and Thompson,[9] using radiation of about 2537A, reported rapid conversion of mercury dimethyl, largely to mercury and ethane, at room temperature, the quantum yield of the process being very nearly unity; these investigators first concluded that at least 90 percent of the metal alkyl decomposed directly to molecular ethane in the primary act, only a small fraction decomposing by way of free radicals. In their second paper they reversed their position and developed a mechanism of decomposition via free methyl radicals which leads to quantum yields higher than unity at elevated temperatures. In studying the analogous decomposition of lead tetramethyl, Leighton and Mortensen[10] held the radical view; in this case, free methyls were detected by the use of lead mirrors, the method being rendered much more sensitive than heretofore by the introduction of a radioactive indicator.

In several instances, the gaseous products resulting from the decomposition of metal alkyls have been analyzed, and the intermediate formation of free radicals has been suggested by the results obtained. Simons, McNamee and Hurd[11] and Paneth, Hofeditz and Wunsch,[12] postulate an initial dissociation of lead tetramethyl into free methyls in order to account for such products as methane, iso-butylene, and a solid carbonaceous deposit. Meinert[13] was led to a similar conclusion on examining the products from the thermal decomposition of lead tetraethyl.

The effect of added hydrogen in the decomposition of metal alkyls has received only brief consideration. It was disregarded by Paneth and Hofeditz in their original investigation,[3] in which hydrogen was used as a carrier gas, but in their later publication[12] interaction between free methyls and molecular hydrogen was postulated to account for the removal as methane of a large fraction of the radicals produced at 900°, and subsequently passed through a tube at 20°. It is significant that the relative extent of methane production was greatly increased by raising the temperature of this tube to 350°. Simons, McNamee and Hurd[11] mention that the addition of hydrogen to lead tetramethyl in a single experiment at 700° increased the proportion of methane produced at the expense of the ethane, and suggest the same explanation.

Hartel and Polanyi[14] have studied the reaction $CH_3+H_2\rightarrow CH_4+H$ by the method of "highly dilute flames," free methyl radicals being liberated in the presence of hydrogen by the action of sodium atoms on methyl halides. From observations of the rate of reaction at two temperatures, they deduced an activation energy of approximately 8 kcal./mole for the reaction. Trenner, Morikawa and Taylor,[1] from their results on the reaction between ethane and atomic hydrogen produced by Wood's method, have suggested 11 kcal./mole as an upper limit.

Experimental Details

Apparatus

Preliminary experiments showed that the decomposition of mercury dimethyl, alone or in the presence of hydrogen, did not involve any change in the total pressure, so the course of the reactions could only be followed by analysis of the products. For reasons outlined below, it was necessary to operate with small samples of gas or vapor, so a special apparatus was constructed. The essential parts are represented diagrammatically in Fig. 1.

Pyrex glass was used throughout, capillary tubing being inserted wherever possible to limit the dead space. V_1 and V_2 were all-metal valves with copper sylphon bellows, their use being necessitated by the readiness with which mercury dimethyl dissolves in grease of any kind, and the experimental procedure was so arranged that these were the only stopcocks with which the vapor came into more than fugitive contact. The mercury dimethyl was stored in A, and because a small amount of Picein was used in the ground

[9] Linnett and Thompson, Trans. Faraday Soc. **33**, 501, 874 (1937).
[10] Leighton and Mortensen, J. Am. Chem. Soc. **58**, 448 (1936).
[11] Simons, McNamee and Hurd, J. Phys. Chem. **36**, 939 (1932).
[12] Paneth, Hofeditz and Wunsch, J. Chem. Soc. 372 (1935).
[13] Meinert, J. Am. Chem. Soc. **55**, 979 (1933).
[14] Hartel and Polyani, Zeits. f. physik. Chemie **B11**, 97 (1930).

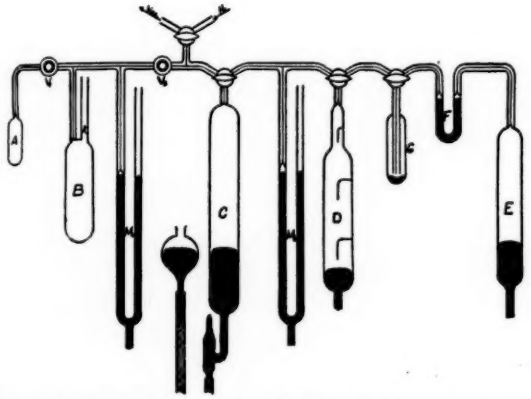

FIG. 1. Apparatus for study of decomposition of mercury dimethyl.

glass joints between the valves and the tubing, it was kept frozen out by means of a carbon dioxide-toluene mixture except for short intervals of time when the samples were being taken. The reaction vessel *B* was of Pyrex for the thermal experiments, and of quartz with quartz-to-Pyrex graded seals for the photochemical; a number of independently calibrated vessels were used, those of Pyrex ranging from 220 to 250 cc, and those of quartz from 115 to 150 cc in volume.

Attempts were first made to heat the sample in vessel *B in situ*, but this was soon found to be impracticable due to the readiness with which the mercury dimethyl distilled into the cooler parts of the connecting tubing and manometer, even with a small temperature gradient. In all the later runs, consequently, the reaction vessel was sealed off after introduction of the sample. After heating or irradiating for a definite length of time, the vessel could then be sealed in place by means of the 10 mm tube shown to the right of the vessel in the diagram. After evacuation, the small glass tip could be broken at will electromagnetically with an iron plunger, and the reaction products thus readmitted to the apparatus.

In the thermal runs, vapor baths containing the following substances were used: aniline, naphthalene, diphenyl, alpha-naphthol, diphenylamine, and anthracene. For the photochemical experiments, a furnace was constructed out of a cylindrical block of aluminum about twice the length of the reaction vessel, and of such diameter that a hole drilled to fit the reaction vessel left walls of 1″ thickness. An aperture the length of the quartz vessel and ½″ in width was cut in one side, covered by a quartz window, and the furnace was wound in such a fashion that the heating element did not cross this window. The furnace was then well covered with asbestos paste, and it was found that, at the highest temperatures used, the temperature did not vary by more than 5° throughout.

The arc used was of the mercury-in-quartz type, operated "hot" at 50 volts and 4 amp. d.c., under which conditions no resonance radiation could be detected; it was operated for fifteen minutes preceding every run in order to attain reproducible intensity, and then placed in a vertical position against the quartz window in the furnace for the duration of the experiment.

Hand Töpler pumps *C* and *E* of approximately 400 and 250 cc capacity, respectively, were used to transfer gas samples from one portion of the apparatus to another. Into a similar vessel *D* were sealed at different levels three glass pointers; by raising the confining liquid to any of these tips, and at the same time setting the level in the connecting arm of manometer M_2 at a standard reading, it was possible to confine a gas sample in a definite volume; these volumes were calibrated with mercury and found to be 33.6, 104.6, and 204.6 cc. Mercury was also used as the confining and manometric fluid throughout.

The bulb *G* of about 50 cc capacity, contained between 1.5 and 2 g of an active copper hydrogenation catalyst, and the U-tube at *F* contained about 5 g of partially-reduced Kahlbaum copper oxide.

The open arms of the manometers were actually connected to the vacuum line (not shown), thereby eliminating the effect of barometric variations; each manometer and hand Töpler pump was provided with a leveling bulb connected through an air-trap as shown for *C*, so that all gas pressures could be read at constant volume.

Materials

The mercury dimethyl used was prepared by the method of Marvel and Gould,[15] and further purified by repeated fractionation at low pressures and in the presence of freshly fused calcium

[15] Marvel and Gould, J. Am. Chem. Soc. **44**, 153 (1922).

chloride. The hydrogen was obtained by the electrolysis at 2–3 amp. of 10 percent potassium hydroxide solution, and passed in succession through calcium chloride, activated charcoal, platinized asbestos at about 250°, and a trap chilled in liquid air. It was not considered necessary to purify the tank helium used to increase the total pressure in a few experiments. The active copper was prepared from Kahlbaum copper oxide by reduction and oxidation at successively lower temperatures, the last reduction being made below 150°; tests on tank ethylene showed rapid hydrogenation below 100°.

Experimental Procedure

Before each experiment, the volume of the particular reaction vessel used, together with the connecting tubing to a set level of the mercury in manometer M_1 was determined by measuring the pressure of a sample of air and then transferring it, by means of C, to the burette D, where its pressure was again measured in a previously calibrated volume. This was usually repeated at the close of the experiment, to determine the increase in volume due to the introduction of the 10 mm tubing containing the "inner seal."

After the sample of air had been pumped out of B, a sample of mercury dimethyl was admitted from A. Due to the readiness with which the material distills and condenses, it was considered advisable to set as an upper limit of mercury dimethyl pressure its vapor pressure at room temperature, which is in the vicinity of 50 mm; in very few cases did the pressure of the metal alkyl significantly exceed 40 mm. With valve V_2 closed and V_1 opened very slightly, the temperature of the vessel A was carefully raised to within a few degrees of that of the room, and the vapor thus allowed to diffuse slowly into B. After standing for some time in a water bath at room temperature, the pressure and temperature of the sample in B were recorded. A sample of hydrogen could similarly be admitted through V_2, the pressure of the hydrogen being maintained high enough to prevent back diffusion of the mercury dimethyl.

To avoid loss or decomposition of the mercury dimethyl while sealing the reaction vessel, it was first immersed in liquid air; this expedient did not prevent a small loss of hydrogen, but this could be estimated by comparing the total pressures before and after the run, as the reaction proceeds without change in the total pressure: moreover, as the hydrogen was always in large excess, the importance of such an error would be minor. The disconnected vessel was then transferred to the vapor bath or furnace, depending on the experiment. In the former, the time of heating was measured from the introduction of the vessel, the time required for it to reach the bath temperature being considered to be offset by that necessary for cooling after its withdrawal; in the photochemical runs, however, the vessel was placed in the furnace for fifteen minutes prior to illumination; it will be seen that the thermal reaction during that period of time at the temperatures used is negligible.

After heating or illumination, the reaction vessel was again connected to the apparatus and the product gases readmitted.

Analysis

The vessel B was immersed in liquid air, and the fraction gaseous at that temperature pumped over, by repeated use of the hand Töpler pump C, into D where its pressure and temperature at known volume were recorded. This gas fraction could consist only of the so-called "permanent gases" methane and hydrogen. The possibility of imperfect fractionation due to solution of these gases in other products in B was investigated by closing V_2, melting and refreezing these products, and again pumping any residual gas over into D: in no case, however, was there observed to be any gas evolved. The hydrogen was removed from the mixture by passing the gases repeatedly over the copper oxide in F at 270–300°, with the mercury leveling bulbs attached to D and E; the residual gas after this operation was measured as methane.

A second gas fraction was transferred from B to D in the same manner, the vessel B being immersed in a carbon dioxide-toluene mixture. This could consist of ethane, propane, and possibly butane, together with the lower members of the unsaturated series. Numerous attempts were made to detect unsaturated hydrocarbons by passing this second gas fraction, together with added hydrogen, over the active copper in vessel G maintained at 100°, but in no case was there any evidence of the pressure decrease which

would attend hydrogenation. Moreover, the observed stoichiometry of the decomposition in the majority of the experiments indicated that propane and butane, if present at all, appeared in negligible amounts, so that the second gas fraction might well be designated as ethane.

The residue in *B*, which probably consisted entirely of undecomposed mercury dimethyl in the majority of the runs, was not transferred from the reaction vessel, but was estimated by its pressure measured on manometer M_1 while the vessel was immersed in a water bath at room temperature. By using this value in conjunction with the directly determined quantities of gaseous products, a satisfactory carbon and hydrogen balance could normally be obtained.

Experimental Results

Thermal decomposition of mercury dimethyl

No measurable decomposition of the metal alkyl alone could be detected after long heating at 184, 215 and 255°. At 290°, gaseous products corresponding to about 2 percent decomposition were observed after five hours heating; at 302°, the rate had increased only very slightly, but when the temperature was raised to 348°, it was relatively rapid.

The course of the decomposition at 348° was followed by heating separate samples for definite periods of time, and the results have been tabulated in Table 1. All the pressures given have been calculated to 0°, only a short extrapolation being involved, as all the actual measurements were made at room temperature. The pressures for the products listed in the last two columns have been recalculated to the volume of the original reaction vessel in each case, for comparison with the values in the fourth column. Appended to the table are two additional runs at 348°, which serve to throw some light on the nature of the decomposition: run 108 shows the effect of decreasing the initial mercury dimethyl pressure, run 109 that of increasing the total surface.

Table I. *Thermal decomposition of* $Hg(CH_3)_2$ *in absence of* H_2.

Temp. °C	Run	Time hr.	Initial $Hg(CH_3)_2$ mm	CH_4 mm	C_2H_6 mm
302	25	2½	21.3	—	1.0
		8	21.6	1.0	1.4
		21½	22.2	2.4	3.2
		30	22.8	5.1	2.9
		41½	23.3	7.7	2.9
348	106	2	37.0	14.2	4.8
	107	4	38.6	22.5	4.0
	105	6	43.3	29.0	5.1
	102	11	47.7	39.1	8.3
	103	21	47.1	39.8	7.3
	108	4	14.8	4.5	2.9
	109[1]	4	46.7	44.3	8.4

[1] Surface increased 8-fold by packing with Pyrex tubing.

A single run at 302° is also reported for comparison, although the accuracy of the data is relatively low. This experiment was performed without detaching the reaction vessel from the apparatus; rough analyses were performed by interrupting the heating, and measuring the total pressure when the vessel was immersed in a water bath, a CO_2 ether mixture, and liquid air. The pressures given, therefore, are obtained by fairly long temperature extrapolations, and serve only as a rough indication of the effect of temperature. It is definitely apparent that the process producing methane shows much greater dependence upon the temperature than does that forming ethane.

In every case in which measurable decomposition took place, it was observed that a dark brown deposit formed on the walls of the reaction vessel. This could be removed to a greater or less extent by washing out with cold water, on the surface of which it formed an oily scum. On gentle heating in the presence of air, the deposit darkened in color, and became definitely carbonaceous. Reference to runs 102 and 103 in Table 1 shows that although decomposition is undoubtedly complete, less than 60 percent of the carbon has been found in the product gases; it would appear that for every carbon atom appearing as methane there is one lost in the solid deposit on the walls. Added evidence for the belief that the deposit might well be a CH_2 polymer is supplied by the experimental fact that no free hydrogen was detected in any run.

Thermal decomposition of mercury dimethyl in presence of hydrogen

In the runs listed in Table II, the initial mercury dimethyl pressures were 40.0±0.2 mm, and those of hydrogen (corrected for loss in

sealing the reaction vessel) 200±4 mm. As in Table I, all pressures are given for 0° and the volume of the reaction vessel. The values in the fourth and fifth columns were obtained by a method of difference, and so are less accurate than those for methane and ethane, which have been measured directly and in smaller volumes. However, the stoichiometry of the reaction producing methane is apparent, one mole of mercury dimethyl and one of hydrogen disappearing in the production of two moles of methane. This indicates that, with the introduction of hydrogen, a new methane-producing process occurs. The absence of any dark deposit at the conclusion of an experiment when hydrogen is present is corroborative evidence.

The presence of hydrogen markedly accelerates the decomposition, which is complete in one hour at 348° instead of eleven, as in the absence of hydrogen. That this effect is not due merely to the increase in the total pressure is shown by the runs using helium. In addition, the methane-producing process in the presence of hydrogen is much less strongly temperature-dependent than that in the case of mercury dimethyl alone, indicating a much lower energy of activation.

Effect of initial pressure

The data of Table III show the influence of reactant pressures at two temperatures. They yield the rate expressions:

at 302°: $d(CH_4)/dt = k(Hg(CH_3)_2)^{0.2}(H_2)^{0.7}$,
at 348°: $d(CH_4)/dt = k(Hg(CH_3)_2)^{0.7}(H_2)^{0.7}$.

TABLE II. *Thermal decomposition of* $Hg(CH_3)_2$ *in presence of* H_2.

Temp. °C	Run	Time hr.	$Hg(CH_3)_2$ used mm	H_2 used mm	CH_4 mm	C_2H_6 mm
302	125	½	9.3	8.8	13.2	—
	126	½	8.1	6.4	12.0	—
	124	1	13.8	11.2	22.0	—
	122	2	23.2	23.6	42.8	—
	123	4	40.1	44.8	80.2	0.7
	130[1]	4½	40.0	—	2.4	—
348	115	½	35.3	31.2	65.0	1.2
	114	1	39.8	39.8	79.3	2.4
	119	1	39.6	38.4	74.9	2.7
	112	2	37.8	37.2	72.0	1.6
	110	4	40.0	40.0	77.6	2.4
	118[1]	½	40.0	—	18.3	1.2

[1] 200 mm helium substituted for hydrogen.

TABLE III. *Variation of initial pressures.*

Temp. °C	Run	Time hr.	Initial $Hg(CH_3)_2$ mm	Initial H_2 mm	CH_4 mm
302	122	2	40.1	199.5	42.8
	127		40.4	100.6	26.9
	129		18.7	185.5	36.6
	128		19.6	98.4	22.2
348	115	½	39.9	198.2	65.0
	120		40.0	100.4	40.1
	121		19.7	195.5	38.6
	117		19.7	98.4	24.0

There is a strong temperature dependence with respect to mercury dimethyl but none with respect to hydrogen.

Experiments at lower temperatures showed erratic behavior indicating surface effects, methane formation increasing with increase of mercury dimethyl, the effect of hydrogen remaining unchanged.

Photochemical decomposition of mercury dimethyl

The data of Table IV record the results of photodecomposition by the unfiltered radiation of a hot mercury arc from 50 to 300°, with an initial pressure of 40 mm of mercury dimethyl. In no photochemical experiment, with or without hydrogen, was any deposit observed to form on the walls of the reaction vessel, with the possible exception of a thin gray film of mercury. No methane was observed in the decomposition of mercury dimethyl below 160°, and it seemed probable that the reaction was free of the undesirable heterogeneous characteristics of the thermal decomposition.

TABLE IV. *Photochemical decomposition of* $Hg(CH_3)_2$ *in absence of* H_2.

Temp. °C	Run	Time min.	$Hg(CH_3)_2$ decomp. mm	CH_4 mm	C_2H_6 mm	C_2H_6/min. mm
50	142	30	11.2	—	10.4	0.35
	144	60	20.4	—	19.7	0.33
	146	90	28.7	—	28.0	0.31
90	152	60	23.2	—	24.6	0.41
160	154	30	20.1	0.1	20.8	0.69
200	168	10	9.3	0.3	7.9	0.79
250	173	6	6.4	0.6	6.2	1.03
275	182	5	5.7	—	4.1	0.82
300	184	3	5.1	1.2	3.4	1.13
	185	3	—	—	2.8	0.93

TABLE V. *Photochemical decomposition of* $Hg(CH_3)_2$ *in presence of* H_2.

TEMP. °C	RUN	TIME MIN.	$Hg(CH_3)_2$ DECOMP. MM	CH_4 MM	C_2H_6 MM	$\frac{1}{2}CH_4+C_2H_6$ MM	CH_4/MIN. MM	C_2H_6/MIN. MM
50	143	30	13.8	4.0	10.4	12.4	0.13	0.35
	145	60	23.2	6.8	19.5	22.9	0.11	0.33
	147	90	(28.7)	11.1	29.3	34.9	0.12	0.33
90	153	60	33.4	10.8	30.2	35.6	0.18	0.50
160	155	30	21.3	8.9	16.1	20.6	0.30	0.54
	159		28.1	13.6	23.8	30.6	0.45	0.79
	160		28.6	16.2	20.9	29.0	0.54	0.70
200	169	10	14.2	10.9	7.8	13.3	1.09	0.78
250	174	6	11.1	12.1	4.1	10.3	2.02	0.70
275	183	5	11.8	11.8	5.0	10.9	2.36	1.00
300	180	3	10.1	12.4	3.2	9.4	4.13	1.07
	181	3	9.9	12.2	2.8	8.9	4.07	0.93

Photochemical decomposition of mercury dimethyl in presence of hydrogen

Addition of hydrogen to the mercury dimethyl was found to result in the production of measurable amounts of methane even at the lowest temperature employed. It was observed, moreover, that the process producing methane showed a much greater dependence upon temperature than that forming ethane, indicating a process of higher activation energy. The rate of ethane production was not affected by the presence of the hydrogen, indicating that the processes producing methane and ethane proceed quite independently of each other. This observation must be given due importance in postulating a mechanism for the decomposition.

In all runs reported in Table V very nearly 200 mm of hydrogen has been added to the mercury dimethyl. The values in the seventh column have been given for comparison with those of the fourth column, to indicate how satisfactory is the carbon balance throughout. It will be observed also from Table IV that the mercury dimethyl decomposed in each run is accounted for within the experimental error.

Special tests, using quartz vessels containing mercury and hydrogen as filters, showed that the effects produced were not due to mercury resonance radiation. It was also shown that a mixture of H_2+D_2 did not react to form 2HD under the experimental conditions. When a "cold" arc was used, the character of the decomposition changed, because of the resonance radiation, methane predominating even at room temperature, because of interaction of the mercury dimethyl and atomic hydrogen produced by photosensitisation with excited mercury.

DISCUSSION OF RESULTS

The primary photo-process, in agreement with Terenin[8] and the later conclusions of Linnett and Thompson,[9] must occur in either of the two following ways

$$Hg(CH_3)_2 \begin{cases} \nearrow HgCH_3+CH_3 \\ \searrow Hg+2CH_3(k_1). \end{cases}$$

The preponderance of methane in presence of hydrogen at the highest temperatures is definite evidence that dissociation to yield mercury and molecular ethane is a minor or negligible result of the absorption act. A choice between the two radical mechanisms cannot be made from the kinetics of the over-all reaction. The complex $HgCH_3$ will, in any case, be of relatively short life.

The ethane formation which preponderates in the low temperature range may be ascribed to the recombination process

$$CH_3+CH_3=C_2H_6(k_4),$$

the rate of production of ethane in absence of hydrogen increases by a factor of 3 in the range 50 to 300° (Table IV). There is no evidence that this can be ascribed to temperature dependence of light absorption, since this is very strong, even at room temperature. The temperature coefficient indicates, therefore, an increase of quantum yield and therefore a chain mechanism, for example,

$$CH_3+Hg(CH_3)_2=C_2H_6+Hg+CH_3,$$

the chain-breaking mechanism being the recombination of two methyl groups. This latter reaction must have a small activation energy since it occurs less rapidly than the recombination of CH_3+I in the photolysis of methyl iodide as indicated by the low quantum efficiency of the iodide decomposition and by the thermal stability of alkyl iodides.[16] The small temperature coefficient of ethane formation must be composite of these two processes.

The data of Tables IV and V show that the ethane producing reactions are not measurably affected by the presence of a large excess of

[16] Ogg, J. Am. Chem. Soc. **56**, 533 (1934).

hydrogen. However, the over-all rate of decomposition of mercury dimethyl is progressively increased, by a 5-fold addition of hydrogen, and approximately in the ratio 1 to 8 between 50 and 300°. An increasingly large proportion of methane appears in the products with increase of temperature. We ascribe this to the following new secondary steps

$$CH_3+H_2=CH_4+H(k_2)$$

and

$$H+Hg(CH_3)_2=CH_4+Hg+CH_3(k_3),$$

this chain being terminated by the recombination of two methyl radicals (k_4).

For a photochemical stationary state

$$d[CH_3]/dt=0=k_1I_{abs}-k_2[CH_3][H_2]+k_3[H][Hg(CH_3)_2]-k_4[CH_3]^2$$

and

$$d[H]/dt=0=k_2[CH_3][H_2]-k_3[H][Hg(CH_3)_2].$$

By subtraction,

$$k_1I_{abs}=k_4[CH_3]^2$$

or

$$[CH_3]=(k_1I_{abs}/k_4)^{\frac{1}{2}}.$$

Substituting these values in the rate expression,

$$\begin{aligned}d[CH_4]/dt&=k_2[CH_3][H_2]+k_3[H][Hg(CH_3)_2]\\&=2k_2[CH_3][H_2]\\&=2k_2(k_1I_{abs}/k_4)^{\frac{1}{2}}[H_2].\end{aligned}$$

If the light absorption is constant, the rate of methane production is independent of mercury dimethyl concentration. The data at 50° in Table V are in agreement with this result. In this formulation of reaction mechanism it is seen that ethane formation is also independent of the hydrogen concentration as observed.

The production of methane in the absence of hydrogen must be ascribed to processes of the types

$$CH_3+Hg(CH_3)_2=CH_4+CH_2.Hg.CH_3$$

$$CH_2.Hg.CH_3 \rightarrow CH_2+HgCH_3$$

$$CH_2.Hg.CH_3 \rightarrow CH_2+Hg+CH_3$$

and

$$CH_3+CH_3=CH_4+CH_2.$$

The large temperature coefficient of thermal reaction between 302 and 348° cannot be attributed to the reaction CH_3+H_2 since this has, as will be shown, a much smaller coefficient. The dark deposit on the reaction walls is evidence of the production of polymethylenic polymerization products. Evans and Lee[17] on studies of the electrolysis of methyl mercuric bromide and Shukla and Walker[18] in electrolysis of fatty acids and their salts postulate methane production by the second of the above processes.

Activation energies of the reactions

If the logarithm of the rates of methane production from Table V be plotted against $1/T$ in the range 160–300° a straight line is obtained whose slope is 8.1 kcal. per mole. As is evident from the expression

$$d[CH_4]/dt=2k_2[CH_3][H_2]$$

this value is a summation of the effect of temperature on the stationary state concentration of methyl radicals and the activation energy E_M of the process $CH_3+H_2=CH_4+H$.

A plot of ethane production, in presence or absence of hydrogen, against $1/T$ gives a single straight line over the entire temperature range the slope of which indicates an activation energy of 1.5 kcal. per mole. As suggested previously, this energy requirement may be attributable to the reaction between free methyl and mercury dimethyl. In such case the effect of temperature on the recombination of methyl radicals whether bimolecularly, or at the wall, must be very small indeed and E_M would be 8.1 kcal. per mole. This latter value would be reduced, if the value of E_E for ethane formation were to be attributed to an activation energy of the recombination process, by the whole amount, 1.5 kcal., in case of a wall recombination, or by 0.75 kcal. for a bimolecular association in the gas phase. These alternatives would set the value for E_M between 6.6 and 8.1 kcal. with the greater weight attaching to the upper figure.

The experimental figures of Hartel and Polanyi[14] led them to a value $E_M=8$ kcal., although a series at 10 mm hydrogen pressure

[17] Evans and Lee, J. Am. Chem. Soc. **56**, 654 (1934).
[18] Shukla and Walker, Trans. Faraday Soc. **27**, 35 (1931).

gave a value of ~6 kcal. In a parallel investigation by Taylor and Rosenblum[19] on the photolysis of acetone in presence of hydrogen the value for E_M deduced on the basis of bimolecular recombination with negligible activation energy is 8.7 kcal., rising to 11 kcal. if the recombination process were unimolecular at the wall. Upon these bases therefore we must conclude that the most trustworthy value now available for the activation energy, E_M, is 9 ± 2 kcal.

[19] H. S. Taylor and C. Rosenblum, J. Chem. Phys. **6**, 119 (1938).

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An Improved Calculation of the Energies of Metallic Li and Na

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The method of calculation used in the present work is a modification of that used by Wigner and Seitz in their original calculations of the energies of metallic Li and Na. The main difference lies in an improved method for the calculation of the Fermi energy. In each polyhedral cell, the wave function of an electron is taken to be of the form $\psi_k=[u_0(r)+i(\mathbf{k}\cdot\mathbf{x})(v_1(r)-u_0(r))]\exp[i\mathbf{k}\cdot\mathbf{x}]$, where $u_0(r)$ and $v_1(r)$ are radial s and p functions, respectively, which depend only on the distance from the ion in the center of the cell. Both functions are determined explicitly from the differential equations, and the energy of the electron is expressed in terms of the boundary values of the wave function. Values of the Fermi energy, and of the total energy of each metal, are tabulated as a function of the lattice spacing. Calculated values of the lattice constants, heats of sublimation, and compressibilities are in fair agreement with experiment.

THE most accurate method for the calculation of metallic binding which has yet been suggested is that of Wigner and Seitz.[1] The method is especially suitable for the monovalent metals, and was first applied to the calculation of the binding energy and lattice constant of sodium. A rough value was also given for the compressibility. Lithium was considered in a later paper by Seitz.[2] His calculation of the energy did not extend to values of the lattice constant smaller than the observed, so that it was not possible to obtain the compressibility. The main object of the present work is to determine the energies of Li and Na and their dependence on volume with sufficient accuracy to obtain the compressibilities and their variation with pressure. A comparison of the results with recent experimental values of Bridgman, which extend to pressures of the order of 45,000 kg/cm², will be given in the following paper.[3]

The two main factors which determine the binding energy of a metal are the energy of an electron in its lowest state and the Fermi energy. Only two electrons can occupy the lowest state; the Fermi energy represents the average additional energy of electrons in higher states of the filled band. We will first give the general theory of the method used for the calculation of the electronic wave functions and energies, and then give the detailed numerical calculations of the binding energies.

Electronic Wave Functions and Energies

The wave function of an electron in its lowest state is determined as follows. By passing planes perpendicular to and bisecting the lines joining near neighbors, the whole space of the crystal is broken up into a set of regular polyhedra, one surrounding each ion. It is a good approximation

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[1] E. Wigner and F. Seitz, **43**, 804 (1933); **46**, 509 (1934); E. Wigner, Phys. Rev. **46**, 1002 (1934). A survey of this work, together with references to applications of the method to other problems may be found in Mott and Jones, *Theory of the Properties of Metals and Alloys* (Oxford, 1936), Chapters II and IV.

[2] F. Seitz, Phys. Rev. **47**, 400 (1935).

[3] A discussion of an approximate method for the calculation of the energies of the alkali metals, due to Fröhlich, is also given in this paper.

to take for the potential in each polyhedron that of the ion in the center of the polyhedron.[4] Since the wave function of an electron in its lowest state has the symmetry of the lattice, its normal derivative must vanish on the surface of the polyhedron. Wigner and Seitz replace the polyhedron by a sphere of equal volume (s sphere), and satisfy the boundary condition on the surface of this sphere. The wave function is then the radial solution of the Schrödinger equation:

$$-(\hbar^2/2\mu)\Delta\psi_0+V(r)\psi_0=E_0\psi_0, \tag{1}$$

subject to the boundary condition

$$(d\psi_0/dr)_{r=r_s}=0, \tag{2}$$

where r_s is the radius of the s sphere. In Eq. (2), $V(r)$ is the potential of a free (positive) ion, and E_0 is the energy of the electron in its lowest state.

The wave function of an electron in a higher state is of the form

$$\psi_k=u_k(x)\exp[i\mathbf{k}\cdot\mathbf{x}], \tag{3}$$

where $u_k(\mathbf{x})$ has the translational period of the lattice. The equation for u_k, obtained by substituting the above in the Schrödinger equation, is:

$$-(\hbar^2/2\mu)(\Delta u_k+2i\mathbf{k}\cdot\operatorname{grad}u_k)+Vu_k=(E_k-\hbar^2k^2/2\mu)u_k, \tag{4}$$

which differs from the equation for u_0 (the wave function of an electron in its lowest state) in the presence of the cross term, $-i(\hbar^2/\mu)\mathbf{k}\cdot\operatorname{grad}u_k$. This term will be small if u_0 is fairly flat throughout most of the volume (free electron case). In any case, it will be small for small k. We may treat this term as a perturbation, and obtain the energy, E_k, to the second order in k, by means of the ordinary Schrödinger perturbation theory.[5] To this order, the energy may be written:

$$E_k=E_0+\alpha\hbar^2k^2/2\mu \tag{5}$$

since the linear term in k is zero. For perfectly free electrons, $\alpha=1$. In general, α may be either greater or smaller than unity.

It is our purpose to determine the value of α. We attempt to solve (4) by a series starting with u_0:

$$u_k=u_0+u_1+u_2+\cdots, \tag{6}$$

where
$$-(\hbar^2/2\mu)\Delta u_0+Vu_0=E_0u_0, \tag{7}$$

$$-(\hbar^2/2\mu)\Delta u_1+Vu_1=E_0u_1+i(\hbar^2/\mu)\mathbf{k}\cdot\operatorname{grad}u_0. \tag{8}$$

We consider only the first-order correction to the wave function, and thus determine the energy to the second order in k. The function u_1 is odd, and, since it is periodic, it will change sign as we pass from one polyhedron into the next. The wave function will therefore be very small on the surface of the polyhedron. It is a good approximation to again replace the polyhedron by a sphere, and to require that u_1 vanish on the surface of the sphere.

Wigner and Seitz find u_1 by the usual perturbation theory, i.e., they expand u_1 in terms of the characteristic functions of the unperturbed equation (7).[6] The solution may be obtained in a much simpler way, if we note that a particular solution of (8) is:

$$u_1=-i(\mathbf{k}\cdot\mathbf{x})u_0(r), \tag{9}$$

as may be verified by direct substitution. To the particular solution, we must add a solution, $i(\mathbf{k}\cdot\mathbf{x})v_1(r)$, of the homogeneous equation in order to satisfy the boundary condition. Thus we take

$$u_1=i(\mathbf{k}\cdot\mathbf{x})v(r)=i(\mathbf{k}\cdot\mathbf{x})[v_1(r)-u_0(r)] \tag{10}$$

and require that

$$v_1(r)=u_0(r) \quad \text{at} \quad r=r_s. \tag{11}$$

There is one solution of the homogeneous equation which is finite at the origin; Eq. (11) determines the scale factor of this solution. Let

[4] It might be better to take instead the potential $V(r)+(3e^2/2r_s)-(e^2r^2/2r_s^3)$. The last two terms represent the potential due to the space charge of the valence electrons in the polyhedron. In order to get the proper value for the interaction energy of the electrons, it would then be necessary to subtract approximately $1.2e^2/r_s$ from the expression for W_s given in Eq. (29). The final value for the total energy would probably be little changed.

[5] An alternative method for the calculation of the energy of electrons in excited states has been given by J. C. Slater, Phys. Rev. **45**, 794 (1934). Slater applied the method to Na; it has been applied to Li by J. Millman, Phys. Rev. **47**, 286 (1935). The entire wave function, $U_k(\mathbf{x})\exp[i\mathbf{k}\cdot\mathbf{x}]$ is expanded in a series of spherical harmonics in each polyhedron, and the boundary conditions are fitted at a number of points on the surface of the polyhedron. The disadvantage of this method lies in the fact that it is necessary to expand the factor $\exp[i\mathbf{k}\cdot\mathbf{x}]$. This may introduce an error even though the potential is flat (cf. W. Shockley, Phys. Rev. **52**, 866 (1937)). The method we have used is, of course, most satisfactory when the wave functions are nearly the same as those of free electrons, which is the usual case for the alkali metals.

[6] See especially F. Seitz, reference 2.

us set

$$u_0(r)=R(r)/r,$$
$$v_1(r)=P(r)/r^2. \quad (12)$$

The equations for $R(r)$ and $P(r)$ are then:

$$d^2R/dr^2+(2\mu/\hbar^2)(E_0-V)R=0, \quad (13)$$

$$d^2P/dr^2-(2/r^2)P+(2\mu/\hbar^2)(E_0-V)P=0. \quad (14)$$

The first is the radial equation for the s function, the second is the radial equation for the p function. These equations must be integrated (in general numerically) to find R and P.

We now want to find the mean value of the energy using the wave function:

$$\psi_k=[u_0(r)+i(\mathbf{k}\cdot\mathbf{x})v(r)]\exp[i(\mathbf{k}\cdot\mathbf{x})]. \quad (15)$$

We have

$$E_k=\int_{\text{cell}}\psi_k^*[-(\hbar^2/2\mu)\Delta+V]\psi_k d\tau. \quad (16)$$

The integration is over one polyhedral cell. The wave function is normalized so that

$$\int_{\text{cell}}\psi_k^*\psi_k d\tau=1. \quad (17)$$

Substituting (15) into (16), and making use of the Schrödinger equation and the normalization condition, we find that we may express E_k, to the order k^2, in the form (5), with

$$\alpha=1+\int u_0[v(r)+(\mathbf{k}\cdot\mathbf{x})^2(kr)^{-2}(dv/dr)]d\tau. \quad (18)$$

After integration over the angular coordinates, we obtain:

$$\alpha=1+4\pi\int_0^{r_s}u_0(r)[v(r)+(r/3)(dv/dr)]r^2dr. \quad (19)$$

Integrating by parts, we may express α in the form:

$$\alpha=1-(8\pi/3)\int_0^{r_s}v(r)(du_0/dr)r^2dr. \quad (20)$$

The integration may be carried out as follows.[7] Let us put (cf. Eqs. (10) and (12))

$$v(r)=P/r^2-R/r \quad (21)$$

and

$$u_0(r)=R/r.$$

With these substitutions:

$$\alpha=1-(8\pi/3)\int_0^{r_s}(P-rR)(dR/dr-R/r)dr. \quad (22)$$

Now

$$\int_0^{r_s}rR(dR/dr)dr=(rR^2)_{r=r_s}-\int_0^{r_s}(R^2-rR(dR/dr))dr,$$

so that, to the approximation we are considering,

$$(8\pi/3)\int_0^{r_s}rR(dR/dr)dr=(4\pi/3)r_s^3[u_0(r_s)]^2-\tfrac{1}{3}.$$

Thus

$$\alpha=(4\pi/3)r_s^3[u_0(r_s)]^2-(8\pi/3)\int_0^{r_s}P(dR/dr-R/r)dr. \quad (23)$$

This result may be expressed in the following form, after a further integration by parts:

$$\alpha=(4\pi/3)\left\{r_s^3[u_0(r_s)]^2-P(r_s)u_0(r_s)+\int_0^{r_s}[R(dP/dr)-P(dR/dr)+2PR/r]dr\right\}. \quad (24)$$

From the differential equations which are satisfied by P and R, we have:

$$R(d^2P/dr^2)-P(d^2R/dr^2)=2PR/r^2,$$

which may be transformed to

$$\frac{d}{dr}\left\{rR\frac{dP}{dr}-rP\frac{dR}{dr}\right\}=R\frac{dP}{dr}-P\frac{dR}{dr}+\frac{2PR}{r^2}. \quad (25)$$

The integration in Eq. (23) can therefore be carried out in terms of the boundary values of the wave functions. Making use of the boundary condition (11), we have, finally,

$$\alpha=\gamma[(r/P)(dP/dr)-1]_{r=r_s}, \quad (26)$$

where $\gamma=(4\pi/3)r_s^3[u_0(r_s)]^2$ is the ratio of the square of the wave function at the boundary of the s sphere to its mean value.

[7] The possibility of carrying out the integration in Eq. (20) in terms of the boundary values of the wave function was pointed out to the author by C. W. Ufford.

Equation (26) provides a very simple method for the calculation of the Fermi energy. But a single integration of the differential equation (14) is required for each value of the lattice constant.

Numerical Calculation of the Energies of Li and Na

According to Wigner and Seitz,[1] the energy of a monovalent metal may be expressed in the following form:

$$W=E_0+F+W_e+W_I. \tag{27}$$

This is the negative of the energy per atom required to break up the metal into positive ions and free electrons, and thus is the sum of the atomic heat of sublimation and the ionization potential. The first two terms represent the value of E_k averaged over all the occupied states; E_0 is the energy of an electron in its lowest state, and F is the additional energy required by the Pauli principle. The next term, W_e, is a small correction to the interaction energy of the electrons (not taken adequately into account in the first two terms) which will be discussed at more length later on. The last term, W_I, is the very small nonelectrostatic interaction energy of the ions (the overlap and van der Waals energies) which we will neglect in the present work.

In order to obtain E_0, it is necessary to find the radial solution of Eq. (1) (or, equivalently, of Eq. (13)), subject to the boundary condition (2). The solutions, $\psi_0(r, E_0)$ which are finite at the origin, depend on two variables, the radial distance r and the energy parameter, E_0. The actual value of E_0 for a given value of r_s is that for which $(d\psi_0/dr)_{r=r_s}=0$. It was desired to find E_0 for a fairly wide range of values of r_s near the energy minimum. In this region, E_0 does not vary rapidly, so that it was possible to obtain accurate values of $\psi_0(r, E_0)$ covering the desired range by integrating Eq. (1) numerically, using but three different values of E_0 for each metal. The values chosen for Li were -0.63, -0.65, and -0.67 Ry, and for Na -0.60, -0.62, and -0.64 Ry. The derivative, $d\psi_0/dr$, for each of these solutions, was obtained by numerical methods. The energy, $E_0(r_s)$, for a given value of r_s, was then obtained by finding, by quadratic interpolation between the three different energies, the value of E_0 for which $(d\psi_0/dr)_{r=r_s}=0$.[8] The same ion-core fields used by Wigner and Seitz were also used in the present calculation.[9] The results are given in Tables I and II for Li and Na, respectively.

Neglecting terms in k^4 and higher order, the Fermi energy is:

$$F=3\alpha\hbar^2k_0^2/10\mu=2.21\alpha/r_s^2 \text{ Ry}, \tag{28}$$

where k_0 is the magnitude of k for the highest occupied state of the Fermi distribution. We have determined α from Eq. (26) after finding $P(r, E_0)$ by numerical integration of Eq. (14). The energies chosen were again -0.63, -0.65, and

Tables I and II. *r_s is the radius of a sphere of atomic volume; E_0 is the energy of an electron in its lowest state; γ is the ratio of the square of the wave function at the boundary of the s sphere to its mean value; α is the effective number of free electrons per atom; F is the Fermi energy $=2.21\alpha/r_s^2$; and W is the total energy per atom. Atomic units (reference 12) have been used.*

Energy of lithium

r_s	$-E_0$	γ	α	F	$-W$
2.36	0.5727	1.179	0.2034	0.0807	0.4501
2.52	.6219	1.165	.3282	.1142	.4717
2.68	.6509	1.151	.4322	.1330	.4869
2.84	.6646	1.134	.5171	.1417	.4964
3.00	.6682	1.114	.5843	.1435	.5022
3.16	.6653	1.094	.6391	.1414	.5048
3.32	.6582	1.072	.6839	.1371	.5049
3.48	.6484	1.050	.7211	.1317	.5031

Energy of sodium

r_s	$-E_0$	γ	α	F	$-W$
3.16	0.6619	1.1294	1.1392	0.2521	0.3907
3.32	.6552	1.1033	1.1165	.2238	.4152
3.48	.6458	1.0779	1.1016	.2010	.4312
3.64	.6346	1.0531	1.089	.1816	.4417
3.80	.6225	1.0287	1.079	.1651	.4482
3.96	.6099	1.0047	1.069	.1507	.4520
4.12	.5972	.9793	1.059	.1379	.4537
4.28	.5846	.9549	1.050	.1266	.4540
4.44	.5722	.9305	1.041	.1166	.4530

[8] An alternative procedure would be to find the values of r_s for which $(d\psi/dr)_{r=r_s}=0$ for each of the three energy values. This would yield six values of $E_0(r_s)$, there being two values of r_s for each energy. One could then interpolate between these values to obtain E_0 for intermediate values of r_s. This procedure is not as satisfactory as the one adopted, because, in the region of interest, interpolation between the different energies for a fixed value of r_s is more accurate than interpolation between different values of r_s for fixed E_0.

[9] The Prokofjew field was used for Na; the semi-empirical field of Seitz was used for Li.

-0.67 Ry for Li and -0.60, -0.62, and -0.64 Ry for Na. From these solutions, values of rdP/Pdr were obtained by numerical methods. Interpolation between these gave the corresponding values for the actual energy, E_0, going with a particular value of r_s. To obtain α, values of $\gamma=(4\pi/3)r_s^3[\psi_0(r_s)]^2$ are also required; these were obtained by numerical integration. Values of γ and α are listed in Tables I and II for Li and Na, respectively. Values of the Fermi energy F, as obtained from Eq. (28), are also given in these tables. It seems to be very difficult to estimate the magnitude of terms in k^4 and higher order in the Fermi energy. They are probably much more important for Li than for Na.

The rapid decrease of the values of α for Li with decreasing r_s in the neighborhood of the normal lattice constant has already been noted by Seitz[2] and by Millman.[5] The decrease continues throughout the range we have considered. The Fermi energy itself decreases below $r_s=3$. Since the Fermi energy does not change rapidly, the normal lattice constant is determined mainly by the minimum of E_0. The Fermi energy of Na is but slightly larger than the free electron value.

If there were never more than one electron in each polyhedral cell, the energy per atom would be E_0+F. To this we must add the correction term, W_e, resulting from the correlations between the positions of the electrons.[10] This correction term is really the sum of three terms: (1) Electrostatic interaction energy of a given electron with other electrons in the same polyhedral cell, assuming no correlation between the positions of the electrons, $(0.6e^2/r_s)$; (2) Exchange energy resulting from the "Fermi hole" between electrons of parallel spin $(-0.458e^2/r_s)$; (3) Energy gain resulting from correlations between the positions of electrons of one spin with those of opposite spin ($\sim -0.58/(r_s+5.1)$ Ry). The values given in parentheses are the free electron values

[10] Cf. Mott and Jones, reference 1, p. 137.

TABLE III.

		Lattice Constant	Heat of Sublimation (Kcal./mole)	Compressibility
Li	(exp.)	3.46A	39[1]	7.4[2]
	(calc.)	3.49A	34	8.4
Na	(exp.)	4.25A	26[1]	12.3[2]
	(calc.)	4.53A	23	12.0

[1] Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, (Reinhold, 1936).
[2] From Bridgman's data (cf. following paper).

which we will use in the present work.[11] Thus, in atomic units,[12]

$$W_e=[0.284/r_s-0.58/(r_s+5.1)]\text{ Ry}. \quad (29)$$

The total energy per atom (experimentally, the ionization potential plus the atomic heat of sublimation) is

$$W=E_0+F+W_e.$$

Values of W for different values of r_s are also given in Tables I and II.

A comparison of the theoretical and experimental values of the lattice constants, heats of sublimation, and compressibilities of Li and Na is given in Table III. The theoretical values for Li are very nearly the same as those obtained by Seitz.[2] The lattice constant of Na is smaller than that obtained by Wigner and Seitz (4.75A) and is in better agreement with experiment. The smaller lattice constant is due to the fact that our values for the Fermi energy do not increase as fast with decreasing r_s as do those used by the above authors. Our calculations permit fairly accurate determinations of the compressibilities, which previously had only been roughly estimated. The variation of compressibility with pressure is discussed in the following paper.

[11] Seitz (reference 2) has shown that, even for Li, the free electron values are close to the actual values.
[12] Unit of length is the Bohr radius, 0.528×10^{-8} cm; the Rydberg unit of energy is equal to the ionization potential of hydrogen (13.5 ev).

Compressibilities of the Alkali Metals

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As a further test of the method of Wigner and Seitz (for the calculation of the energies of the monovalent metals), the pressure variation of the compressibilities of the alkali metals is determined and compared with recent experimental results of Bridgman which extend to pressures of the order of 45,000 kg/cm². Fröhlich's approximate analytic expression for the dependence of the energies of the alkali metals on volume suggests the following semi-empirical form:

$$W=a/v+b/v^{\frac{1}{3}}-c/v^{\frac{1}{2}}.$$

If the parameters are determined from (1) the lattice constant, (2) the energy, and (3) the compressibility (all at zero pressure), the expression gives values for the relative change in volume with pressure in close agreement with Bridgman's results. The constants so determined agree fairly well with Fröhlich's theoretical values. Compressibilities of Li and Na, as obtained from the more exact and fundamental calculations of the energies given in the preceding paper, are compared with the experimental values. Theoretical values for Na are in good agreement with experiment, but the corresponding values for Li are about fifteen percent too high. It is suggested that the polymorphic transition in Cs, which occurs at a pressure of about 22,000 kg/cm², is a transition from the normal body-centered to a face-centered form, resulting from the nonelectrostatic interaction energy of the ions, which favors close packing.

I. INTRODUCTION

BRIDGMAN[1] has recently obtained rough experimental values of the compressibilities of a large number of the more compressible substances in the pressure range extending to about 45,000 kg/cm². Of particular theoretical interest are the results he obtained for the alkali metals. Thanks largely to the work of Wigner and Seitz,[2] it is possible to make fairly accurate calculations of a large number of properties of this particular group of metals. A calculation of the compressibility and its variation with pressure provides a very sensitive test of the general methods.

The instantaneous compressibility, K, of a metal at the absolute zero of temperature is determined from the energy, W, by means of the following equation:

$$1/K=-v(dp/dv)=v(d^2W/dv^2), \qquad (1)$$

where v is the volume of the metal and p is the pressure. Our problem is thus the calculation of the energy of a metal as a function of volume.

We have given, in the preceding paper,[3] a calculation of the energies of Li and Na. In Section III of the present paper, we discuss the compressibilities and their variation with pressure. Fröhlich[4] has given an approximate expression for the energy of an electron in its lowest state. Using the free electron value for the Fermi energy, he has determined the initial compressibilities of the alkali metals, and obtained rough agreement with experiment. A modification of Fröhlich's procedure is discussed in Section II. At the end of the paper, we give a brief discussion of the polymorphic transition in Cs, discovered by Bridgman.

II. SEMI-EMPIRICAL CALCULATION OF THE VARIATION OF THE COMPRESSIBILITY WITH PRESSURE

In the present section we assume that the energy of the metal (per atom) is the sum of the energy of an electron in its lowest state, E_0, and the Fermi energy, F. We neglect the small correction term to the interaction energy of the valence electrons (given by Eq. (29), reference 3) and also the nonelectrostatic interaction energy of the ions.

According to Fröhlich,[4] for values of r_s near the energy minimum (or, in the neighborhood of the normal lattice constant), the energy E_0 (in atomic units[5]) is given by the following

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[1] P. W. Bridgman, Proc. Am. Acad. **72**, 207 (1938).

[2] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934). E. Wigner, Phys. Rev. **46**, 1002 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935).

[3] In the present issue. This paper will be referred to as (I).

[4] H. Fröhlich, Proc. Roy. Soc. **158A**, 97 (1937); *Electronentheorie der Metalle* (Berlin, 1936) p. 272.

[5] Unit of energy is the Rydburg (13.5 ev); unit of length is the Bohr radius (0.528×10^{-8} cm).

approximate expression,

$$E_0 = a/r_s^3 - 3/r_s, \tag{2}$$

where r_s is the radius of a sphere of atomic volume (s sphere). The repulsive energy is inversely proportional to the atomic volume, and the attractive energy, resulting from the interaction of the valence electrons with the positive ions is inversely proportional to the lattice constant.

The assumptions on which this formula is based are not very clear from Fröhlich's treatment. It is not difficult to show that (2) follows if

$$\gamma = (4\pi/3) r_s^3 [\psi_0(r_s)]^2 = 1, \tag{3}$$

or, in other words, if the value of the wave function at the boundary of the s sphere is equal to its mean value. This relation must hold for all values of r_s for which (2) is to be applied. One would expect that (3) will be approximately satisfied if the wave function of an electron in its lowest state is fairly flat throughout most of the volume. There is reason to suppose that this will be the case for values of r_s near the actual atomic radius, since both $(d\psi_0/dr)_{r=r_s}$ and $(d^2\psi_0/dr^2)_{r=r}$ vanish when E_0 is a minimum.[6]

To derive (2) from (3), let us set $R = r\psi_0$, so that the Schrödinger equation for R (in atomic units) is:

$$d^2R/dr^2 = (V(r) - E_0)R. \tag{4}$$

The potential $V(r)$ is that of a free (positive) ion. The boundary condition of Wigner and Seitz[2] is:

$$dR/dr = R/r \quad \text{at} \quad r = r_s. \tag{5}$$

Both E_0 and R are functions of r_s, the point at which the boundary condition (5) is to be satisfied. Denoting derivatives with respect to r_s by a prime, we have, differentiating (4),

$$d^2R'/dr^2 = (V(r) - E_0)R' - E_0'R, \tag{6}$$

so that, multiplying by R, integrating, and making use of (4) to eliminate $(V - E_0)RR'$, we obtain:

$$E_0' \int_0^{r_s} R^2 dr = \int_0^{r_s} [R'(d^2R/dr^2) - R(d^2R'/dr^2)]dr$$
$$= [R'(dR/dr) - R(dR'/dr)]_{r=r}. \tag{7}$$

[6] For a discussion of this point, see N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys*, (Oxford, 1936), p. 79. Values of γ for Li and Na are tabulated in (I).

Differentiating the boundary condition (5) with respect to r_s, we have:

$$[(d^2R/dr^2) + (dR'/dr)]_{r=r_s} = [R'/r]_{r=r_s}. \tag{8}$$

Making use of this relation, we can eliminate R' from (7) and obtain

$$E_0' \int_0^{r_s} R^2 dr = [R(d^2R/dr^2)]_{r=r_s}$$
$$= [V(r_s) - E_0(r_s)]R(r_s)^2. \tag{9}$$

We thus get the following differential equation for E_0, if condition (3) is satisfied:

$$dE_0/dr_s = (3/r_s)[V(r_s) - E_0(r_s)]. \tag{10}$$

Fröhlich's result (Eq. (2)) is obtained by integrating (10) with $V(r_s) = -e^2/r_s$. The latter will hold for values of r_s larger than the radius of the ion core.[7]

It is, of course, impossible to tell *a priori* whether or not Fröhlich's formula will hold without making an explicit calculation of the wave functions using the actual potential of the ion, as Wigner and Seitz have done for Na and Li. Eq. (2) does give fairly good values for these metals. We will use, for comparison with the experimental data (of all the alkali metals) an expression of the form:

$$E_0 = a/r_s^3 - c/r_s, \tag{11}$$

treating a and c as empirical constants. The value of c so obtained is then compared with the theoretical value (3) given by Eq. (2).

The Fermi energy F, expressed in atomic units, is

$$F = 2.21\alpha/r_s^2, \tag{12}$$

where α is the effective number of free electrons per atom. If the electrons are free, α is equal to unity. In general, α may be either greater or smaller than unity, and may be a function of r_s. It is known that the value of α for Li is much less than unity, and decreases as r_s decreases, while for Na, α is slightly greater than unity and increases slowly as r_s decreases.[8] As a first approximation, we may assume that $\alpha = 1$, so that the Fermi energy will be inversely proportional to the square of the lattice constant.

[7] The author is indebted to Professor E. Wigner for a discussion of Fröhlich's formula.

[8] Tables I and II, reference (I).

Equations (11) and (12) suggest the following type of equation for the energy of an alkali metal:

$$W=A(v_0/v)+B(v_0/v)^{\frac{1}{3}}-C(v_0/v)^{\frac{1}{3}}, \quad (13)$$

where A, B, and C are independent of the volume, and v_0 is the atomic volume at zero pressure. The first and third terms come from the energy of an electron in its lowest state; the second from the Fermi energy. To determine the values of the three parameters, the following experimental data are used (all refer to 0°K and $p=0$):

(1) The lattice constant;

(2) The energy, given by the sum of the ionization potential and the atomic heat of sublimation, and

(3) The compressibility, K_0.

The values of the constants so obtained are checked in two ways. First, the empirical values of B and C are compared with the theoretical values given by Eqs. (12) and (2). The semi-empirical equation is then used to determine the change in compressibility with pressure (or, what amounts to the same thing, the relative change in volume with pressure) and the calculated values are compared with experiment.

Since the energy is a minimum when $v=v_0$ (or $p=0$) we have:

$$2C/3=2A+4B/3. \quad (14)$$

The energy at zero pressure is given by:

$$-W=2A+B. \quad (15)$$

Finally, the compressibility at zero pressure gives the relation:

$$3/K_0=2A+2B/3. \quad (16)$$

To obtain (15) and (16) we have used the value of C given by Eq. (14).

Table I gives the relevant data for the calculation of A, B, and C for the alkali metals. Row (d) gives the energies, obtained from the sum of the ionization potential and the atomic heat of sublimation. The compressibilities, given in row (e) were obtained by extrapolating the experimental results, taken at room temperature, to $T=0$°K by means of the Debye equation of state, as discussed below. From the values given in these two rows, the constants A and B were determined by use of Eqs. (15) and (16); the results are given in rows (f) and (g). Row (i) gives the values of $\frac{2}{3}C$ obtained by substituting these values of A and B into Eq. (14). Row (h) gives the theoretical values of B as obtained from Eq. (12) under the assumption that $\alpha=1$ (free electron value). Row (k) gives the theoretical values of $\frac{2}{3}C$ obtained from Eq. (2) of Fröhlich.

The empirical values of B, depending on the small difference between rows (d) and (e), are not at all accurate, but they are rather small for all metals except Li. The anomalous value for Li results from the fact that α is not constant, but decreases as the volume decreases. The Fermi energy cannot be expressed as a single term, but is given in fair approximation in the region of interest by the difference between a large positive term inversely proportional to the square of the lattice constant, and a negative term inversely proportional to the volume. The negative value of B obtained for K may perhaps be explained in a similar fashion. The differences between the theoretical and experimental values of B for Na, Rb and Cs, are probably within the rather large experimental uncertainties.

A much more significant test of the theory is obtained from a comparison of the empirical and theoretical values of C given in rows (i) and (h). The agreement is good for all metals except K, for which the empirical value is somewhat smaller than the theoretical.

As a second (experimental) test of the semi-empirical equation (13), we compare the relative

TABLE I. *Calculation of the parameters in the semi-empirical equation for the energies of the alkali metals:* $W=A(v_0/v)+B(v_0/v)^{2/3}-C(v_0/v)^{1/3}$. *The theoretical values of B are obtained from the free electron formula for the Fermi energy; theoretical values of C are obtained from Frohlich's formula for the energy of an electron in its lowest state. Units: row a,* 10^{-24} *cm³; rows b and c, ev/atom; rows d to j,* 10^{-12} *erg/atom.*

	METAL	Li	Na	K	Rb	Cs
a	Atomic Volume (v_0)	20.7	38.5	71	86	107
b	Ionization Potential	5.37	5.12	4.32	4.16	3.9
c	Heat of Sublimation[1]	1.70	1.13	0.86	0.82	0.82
d	$-W_0$	11.2	9.8	8.2	7.9	7.5
e	$3v_0/K$[2]	8.4	9.4	8.9	8.1	7.5
f	A(emp.)	1.4	4.3	5.1	4.2	3.7
g	B(emp.)	8.4	1.2	−2.1	−0.6	0.0
h	B(theor.)	4.5	3.0	2.3	1.7	1.5
i	(2/3)C(emp.)	13.9	10.3	7.5	7.6	7.5
j	(2/3)C(theor.)	13.2	10.8	8.8	8.2	7.6

[1] Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, (Reinhold, 1936).
[2] From Bridgman's data, extrapolated to $T=0$°K.

change in volume with pressure given by the theory, with the experimental values of Bridgman.[1] It is first necessary to extrapolate the observed values to $T=0°K$. To do this, we use the Debye equation of state,[9] although it probably does not apply accurately to the alkali metals. The Debye equation is:

$$p=-(dW/dv)-3kT(d\theta/\theta dv)D(\theta/T). \quad (17)$$

Here W and v are the energy per atom and the atomic volume, respectively, and θ is the characteristic temperature. The function $D(x)$ is defined by:

$$D(x)=\frac{3}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^\xi-1}. \quad (18)$$

For small x (T large), $D(x)\simeq 1$. The value of $d\theta/dv$ is obtained from Grüneisen's law:

$$3\alpha/K=-(d\theta/dv)(c_v/\theta), \quad (19)$$

in which α is the linear coefficient of thermal expansion,* K is the compressibility, and c_v is the atomic heat capacity:

$$c_v=3k[D(\theta/T)-(\theta/T)D'(\theta/T)]. \quad (20)$$

Using (19) and (20), we have, for small values of θ/T,

$$p=-(dW/dv)+\Delta p, \quad (21)$$

where

$$\Delta p=(3\alpha T/K)[1-(3\theta/8T)+(1/10)(\theta/T)^2-\cdots]. \quad (22)$$

The second term of Eq. (21), Δp, represents the pressure due to the thermal motion of the ions, which must be subtracted from the observed pressures (at room temperature) to obtain the pressure at $T=0°K$. Although this term depends on the volume, the change is probably not very great except at very high pressures. In this region, the correction term is but a small fraction of the total pressure. We have therefore assumed that Δp is independent of volume, and to determine its value we have used the values of α, K, and θ for zero pressure and room temperature. Table II gives the values of Δp for the alkalis, together with the relevant data used in the calculation. The total relative change in volume due to thermal expansion from room temperature down to $T=0°K$ is also given.

A plot of the relative change in volume of the different alkalis as a function of pressure is given in Fig. 1. The heavier lines represent the experimental values extrapolated to the absolute zero of temperature; the lighter lines are the theoretical values obtained from the semi-empirical formula (13). From this equation we find

$$pv_0=y^4(y-1)[2A+\tfrac{2}{3}B+A(y-1)], \quad (21)$$

with $$y=(v_0/v)^{\frac{1}{3}}.$$

The values of A and B which were used are given in rows (f) and (g) of Table I.

The agreement is good for all metals except Rb. Professor Bridgman informs me that the initial compressibility for this metal is less certain than for the other alkalis. The initial compressibilities were used in the determination of the parameters, so that the slopes of the theoretical curves agree with the slopes of the experimental curves at the origin. It is the shape of the curve which is important for a test of the validity of the theory. The shape is determined mainly by the factor $y^4(y-1)$ in Eq. (21). (The term $A(y-1)$ in the brackets is small.)

There is a tendency for the theoretical curves to be slightly above the observed at the highest pressures. The nonelectrostatic interaction energy of the ions, which we have neglected, is not large enough to account for this discrepancy. The general agreement would have been better if the parameters had been adjusted to make the experimental and theoretical curves match at some high pressure, rather than to fit the initial compressibilities.

III. Compressibilities of Li and Na

It is much more desirable to have a calculation which is based on fundamental principles, so that there are no parameters to be determined from experiment. In order to determine the compressibility and its variation with pressure, it is necessary to have an accurate calculation of the energy as a function of volume. Such a calculation for Li and Na is given in the preceding paper.[3] In Fig. 2, we show the theoretical curves

[9] See, for example, J. K. Roberts, *Heat and Thermodynamics* (Blackie, 1933).

* Not to be confused with the effective number of free electrons per atom, for which the same symbol has been used.

of the compressibilities as a function of volume, as determined from these energy values. For comparison, experimental curves derived from Bridgman's data,[1] extrapolated to $T=0°K$, as indicated above, are also given. The abscissa gives the relative change in volume from the observed volume at zero pressure. The smallest volumes correspond to a pressure of about 40,000 kg/cm². The curves for Na are in very good agreement, but the theoretical values for Li are about 15 percent too high. The difference in the latter case is perhaps due to our neglect of terms of higher order than those in k^2 in the calculation of the Fermi energy.

The reciprocal of the compressibility is given essentially by the second derivative of the energy with respect to volume. It is interesting to note that the second derivative of the Fermi energy of Li is negative, and that the main contribution to $1/K$ comes from the energy of an electron in its lowest state, E_0. On the other hand, the second derivative of E_0 is small for Na, and the main contribution comes from the rapid increase of the Fermi energy with decreasing volume.

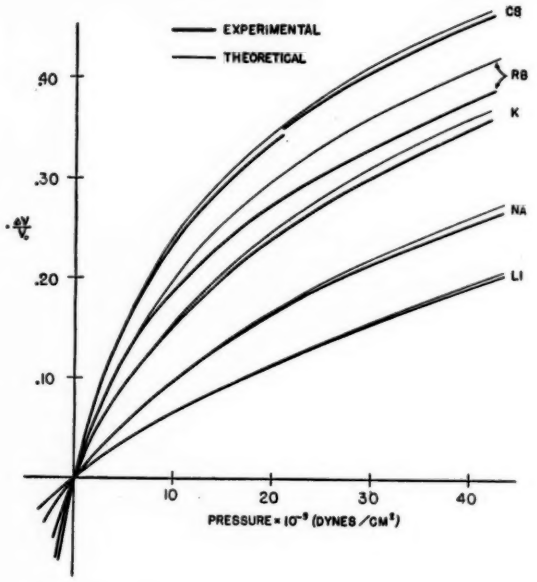

FIG. 1. Relative change in volume of alkali metals with pressure. Light lines are theoretical values obtained from the semi-empirical equation (13). Bridgman's experimental data, extrapolated to $T=0°K$, are represented by the heavy lines. The initial compressibilities have been used to fix the values of the parameters in the semiempirical equation, so that the slopes of the experimental and theoretical curves are in agreement at the origin. The break in the curve for Cs is due to a polymorphic transition.

IV. Polymorphic Transition in Cs

At ordinary pressures, the alkali metals are body centered. It is not yet known why this structure is preferred over, for example, the close packed cubic structure (face centered). Fuchs[10] has shown that, for equal atomic volume, the energies of the valence electrons in the two structures differ by only about 10^{-3} ev per electron. He attributes the face-centered structure of the noble metals (Cu, Ag and Au) to the repulsion between the closed d shells of the ions, which naturally favors the close packing. The nonelectrostatic energy of the ions in the alkali metals (resulting both from the exchange repulsion and the van der Waals energy) will also be lower in a face-centered lattice than in a body-centered lattice, but this energy is so small at ordinary pressures that it has little influence on the structure. As the volume is decreased, the energy of the ions will increase relatively to the energy of the valence electrons, so that one would expect that at very high pressures the alkali metals would take up a close packed structure. The rare gas solids are, of course, face centered, and it is likely that the alkali metals are also face centered at very high pressures.

TABLE II. *Data used in the extrapolation of Bridgman's results to $T=0°K$.*

Metal	Li	Na	K	Rb	Cs
$\alpha\times10^6$	5.6	7.1	8.3	9.0	9.7
$(1/K)\times10^{-9}$ (dynes/cm²)	120	58	32	23	19
θ/τ	1.5	0.6	0.40	0.29	0.20
$\rho\times10^{-9}$ (dynes/cm²)	3.5	2.8	2.0	1.6	1.5
$\frac{v_\tau - v_0}{v_0}$ (calc.)	0.031	0.043	0.060	0.080	0.084

[10] K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935).

The metal for which the transition should take place at lowest pressure is Cs, since it not only has the largest ion of the alkali metals, but also has the highest compressibility. Bridgman has found a polymorphic transition in Cs at a pressure of about 22,000 kg/cm². The change in volume at the transition point is 0.00336 cm³/g, and the latent heat, determined from the change in transition pressure with temperature is 8.49

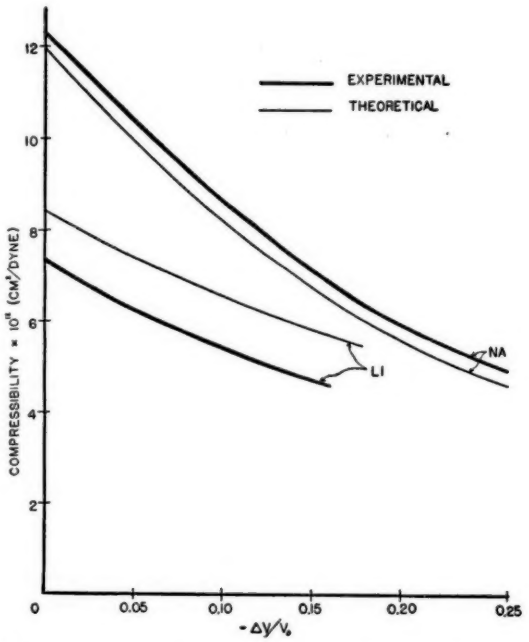

FIG. 2. Compressibilities of Li and Na as a function of pressure. Theoretical values are obtained from direct calculations of the energies (given in the preceding paper); experimental from Bridgman's data, extrapolated to $T=0°K$.

kg cm/g (0.2 cal./g). The small latent heat shows that the difference in entropy between the two phases is small.

A rough test of the theory that the transition is due to the nonelectrostatic energy of the ions may be obtained from the change in volume at the transition point. Let the free energy of the low pressure phase be $F_1(v)$ that of the high pressure phase be $F_2(v)$, and the corresponding volumes at the transition point be v_1 and v_2. Expressing the condition that the pressures of the two phases are equal at the transition point, we have, for v_1-v_2 small,

$$\left[\frac{d(F_1-F_2)}{dv}\right]_{v=v_1}=\frac{v_1-v_2}{v_1}\left(\frac{1}{K_1}\right)_{v=v_1}, \qquad (22)$$

where K_1 is the compressibility of the low pressure phase. The right-hand side may be evaluated from experimental data. The result is 0.83×10^9 dynes/cm².[11] In order to obtain a rough theoretical value for the left hand side of the equation, we will assume that the main contribution comes from the difference in the repulsive energy of the ions in the two phases. The difference in energy of the valence electrons, which presumably favors the body-centered lattice, will not change rapidly with volume, so that the derivative will be small. If we assume that the van der Waals energy of the ions varies as $1/r^6$, the difference between its values for the body-centered and face-centered structures is very small.

The exchange repulsion between the alkali ions has been estimated by Mayer and collaborators[12] from an analysis of the alkali-halide crystals. They find, for the mutual repulsive energy of two ions a distance r apart,

$$W=A_i \exp\left[(2r_i-r)/\rho\right], \qquad (23)$$

where, if A_i is taken to be 1.25×10^{-12} ergs, the ionic radius $r_i=1.455$A for the Cs ion, and $\rho=0.345$A for all the alkali and halide ions. Using these values, we have estimated the contribution of the repulsion of the ion cores to (22) and find a value which is only about one-fifth of that observed. However, direct calculations[13] of the repulsion between the rare gas atoms He and Ne show that the energy can be given approximately by the form (23), with $\rho=0.21$A, a value much smaller than that of the above authors. The larger value probably results from the fact that it is a kind of a mean between the values for the alkali ions and the halide ions, and the latter are probably much larger than the former. If we take $\rho=0.21$A for the Cs ion, and take the same value for $A_i(1.25\times10^{-12}$ ergs) we estimate, from the lattice constant of the corresponding rare gas solid, that $r_i\sim1.75-1.80$A. With these values, one obtains results of about the right order of magnitude for (22).

Due to the difficulties in estimating the difference between the energies of the valence electrons in the two different structures, and also to the difficulty in estimating the interaction energy of

[11] This value is for room temperature. In order to compare with theory, we should take the value at absolute zero. Without a knowledge of the thermal expansion in the two phases, the change with temperature cannot be determined, but it is probably not very great. As we are interested only in the order of magnitude, we use the room-temperature value.

[12] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932); M. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

[13] J. C. Slater, Phys. Rev. **32**, 349 (1928) (He); W. E. Bleik and J. E. Mayer, J. Chem. Phys. **2**, 252 (1934) (Ne).

the ions, one cannot be certain, but it does seem probable that the transition in Cs is from a body centered to a more close packed structure, which is probably face centered.

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Electronic Structure of the First Row Hydrides

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Stehn's formulae for the energies of the first row hydrides, BH to FH, in terms of Heitler-London exchange integrals have been applied to more recent data. The empirically derived values for the integrals are now smooth functions of the atomic number, Z. They are also considered as functions of the internuclear distance, r_e, and taken in conjunction with data on BeH, and with the facts that r_e and the force-constant, k, are smooth functions of Z, but invariant to electronic excitation, the results show that it is $2s^2-1s$ exchange that predominates in fixing the internuclear distance and force-constant. On the contrary, the dissociation energies cannot be expected to be smoothly dependent on Z, r_e or k. The heat of dissociation of NH is calculated by Stehn's formulae, after interpolating one exchange integral.

Introduction

PRESENT theories of heats of dissociation of molecules with more than four electrons are quite crude, and any correlation between theory and experiment, even for the simplest molecules would have value in giving theoretical thermochemistry a better quantitative basis. Stehn [1] made a considerable contribution in deriving formulae for the energies of the first row hydrides, BH, CH, NH, OH, FH, in terms of exchange and Coulomb integrals which can be determined empirically and tested for self-consistency. Since his publication new data have appeared, and in this paper the integrals are recalculated. The three classes of integrals are now smooth functions of the atomic number, and combined with facts known about the internuclear distances and force-constants give a more detailed picture of the orbitals in these molecules.

Redetermination of the Integrals

Stehn applied the usual Heitler-London theory, building the molecules from a hydrogen $1s$ electron and various configurations of the heavy atom, to obtain expressions for the electronic energy

$$W=A+a_1B+a_2K+a_3J_\pi+a_4J_\sigma, \qquad (1)$$

where A is the atomic level of the heavy atom into which the molecule adiabatically decomposes, B is an atomic exchange integral, K the exchange of the hydrogen $1s$ electron with s electrons plus Coulomb terms, J_π and J_σ the exchange with π or σp electrons. The a's are numerical coefficients of the matrix elements. Stehn noticed that the internuclear distance remains practically the same in all excited states of any one molecule, so that the J's and K remain the same, permitting simultaneous equations in them to be set up and solved. In this application then the principal defect of the Heitler-London method, that of nonorthogonality, cancels out; but other corrections, such as higher order terms destroy the linearity of Eq. (1).

Discussion of the Data

The excitation energies ν_{mol} and ν_{atom} are usually known quite accurately, and sometimes the J integrals can be calculated from them alone. But a complete solution also depends on one dissociation energy, which is invariably the weakest datum. However, for any one molecule only one

* National Research Fellow in chemistry.
[1] J. R. Stehn, J. Chem. Phys. **5**, 186 (1937).

such energy need be known, by virtue of the well-known cycle connecting upper and lower level dissociation energies, D_e' and D_e'',

$$\nu_{\text{mol}}+D_e'=\nu_{\text{atom}}+D_e''. \qquad (2)$$

The literature on the dissociation energies of this series of hydrides has been investigated thoroughly. In our calculations we have not used any approximate D's, e.g., from the formula $\omega_e^2/4x_e\omega_e$, or from extrapolation to the limiting vibrational quantum numbers, but only those obtained from dissociation through rotation, which gives an upper *and a lower* limit to D_e, (BH, CH), or from thermal data, (OH, FH).

Further details

An error in D for CH or NH will not change the values of their J_π or J_σ, which are obtained from the ν's. The CH datum is reliable, so K of CH is a good point, Fig. 1. There is not enough data for the evaluation of all three integrals in the case of BH. However, if J_σ of BH is taken to fit in with J_σ of C, N, OH, then J_π automatically will fit in with J_π of C, N, OH, and K will fit with the K's of CH and OH. Since J_σ and J_π of NH fall smoothly on their respective curves, we can expect to interpolate K of NH.

There is no value for the heat of dissociation of NH; but in the appendix we show this interpolated value of K is probably very good.

The heat of dissociation of FH can only be obtained with the help of thermochemical data. Three investigators report[2] a heat of formation of +63.0 kcal. To get the dissociation energy of FH, the dissociation energy of F_2 is also needed. This has been evaluated as −62.6 kcal. by Franck's method from the onset of continuous absorption in the spectrum.[3] This value can be verified from spectroscopic constants[4] as follows:

The upper state of F_2, $^1\Pi$, has an $\omega_e=837$ cm^{-1} and anharmonicity $x_e\omega_e=140$. The formula $\omega_e^2/4x_e\omega_e$ gives a value of D_e that is usually too high, but the absolute error in this case is very small, of the order of magnitude of D_e' itself, 0.155 ev. Mulliken[5] has shown that the upper state dissociates into normal atoms. Hence the dissociation energy of the lower state, D_e'',(which cannot be reliably determined by $\omega_e''^2/4x_e''\omega_e''$), is $D_e'+\nu_{\text{mol}}$ $=0.155+2.575=2.73$ ev or 63 kcal, as above. The D_e for HF then is 6.35 ev.

Kirkpatrick and Salant[6] obtained bands with high vibrational quantum numbers in the infra-red, and extrapolated to get $D_e''=6.1$ ev.[7]

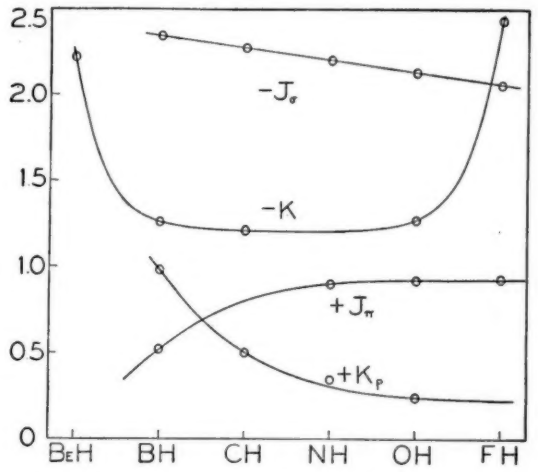

FIG. 1. Values in electron volts of the exchange integrals J_π and J_σ, the total Coulomb terms plus $2s^2-1s$ exchange K, and the $2p-1s$ Coulomb term K_p, as functions of the atomic number.

DISCUSSION OF THE INTEGRALS

The solutions obtained for J_σ, J_π, and K are plotted against the atomic number Z in Fig. 1, and against the internuclear distance in Fig. 2. The principal remark is that the integrals are fairly constant for the series and that the curves are quite smooth. The values for K especially have become less erratic than in Stehn's figure, and show less variation. The fact that fairly constant values are obtained, even though the internuclear distance has changed markedly (from a constriction of the wave functions with increasing Z) shows that overlapping occurs to nearly the same extent and in the same relative positions.

The integral J_σ is large, as to be expected. As will be shown below the equilibrium distance is fixed by $2s^2-1s$ interchange. The minimum of J_σ is beyond this point, because the radius, and also the maximum value, of a $2p$ electron in a "dumbbell" orbital is larger than that of the $2s$ electron. The relative positions of the minima of $1s-2s$ and $1s-2p$ exchange can also be

[2] Bichowski and Rossini, *Thermochemistry of Chemical Substances* (1937).
[3] von Wartenburg, Sprenger and Taylor, Zeits. f. physik. Chemie, Bodenstein Festschrift, 61 (1931).
[4] Sponer, *Molekulspektren I*, p. 18.
[5] R. S. Mulliken, Phys. Rev. **36**, 701 (1930)
[6] D. E. Kirkpatrick and E. O. Salant, Phys. Rev. **48**, 945 (1935).
[7] Landolt-Börnstein, *Tabellen*, Vol. 3, p. 2873, state thermochemical data gives $D_e''=120$ kcal. or 5.2 ev, but this probably was old thermal data, ibid. Vol. 2, p. 1489, uncorrected for polymerization, ibid., Vol. 3, p. 2746 and also Bichowski and Rossini, reference 2.

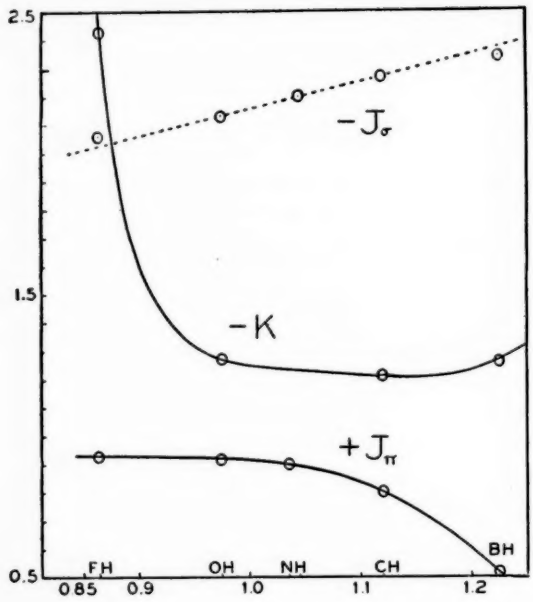

FIG. 2. Values of the integrals J_π, J_σ and K as functions of the internuclear distance. The dotted curve represents J_σ as calculated from Rosen's expression for this integral.

estimated from the integrals derived by Rosen.[8] The J_σ integral is quite flat, so that the points on Figs. 1 and 2 are very close to the maxima of this integral.

The second-order effect, the slight *increase* of J_σ with increasing r_e can also be accounted for by simple exchange integral theory. Rosen evaluated the integral between a $2p$ and a $1s$ electron, which is, except for $1/r_{12}$ terms,

$$J_\sigma = NZ_1^2 r_e(Z_1 r_e+1)e^{-Z_1 r_e}, \tag{3}$$

N being unity minus a nonorthogonality function, fairly independent of Z_1. In this derivation both nuclei are supposed to have the same charge Z_1. Since the heavy nucleus is heavily shielded in these molecules, (3) should not be a bad formula for comparisons. It can in fact be fitted to the straight line of J_σ *versus* r_e of Fig. 2 by two parameters, the "constant" N and a shielding constant of 0.63 for each p electron on the p electron that is exchanging. Usual values of shielding of $1s^2 2s^2$ were taken,[9] but the calculations are insensitive to them. Shielding constants are discussed again later. The same value is obtained assuming Z_1 to be the average of the effective charge of the heavy nucleus and proton, indicating (3) may be fairly good even when there is asymmetry.

The integral J_π *decreases* with increasing r_e, and quite suddenly farther out, as would be expected of overlapping of the hydrogen $1s$ with π electrons. As r_e decreases to form the united atom, J_π becomes an atomic exchange integral between a $2p_\pi$ and a $2p_\sigma$ electron, equal to $3F_2$ (Shortley-Condon notation). An extrapolated value of $3F_2$ through C, N, O, F, is just about the value of 0.94 ev to which J_π of Fig. 2 converges.

The quantity K is actually a sum of several terms; the exchange and Coulomb integrals of $2s^2-1s$ binding, say K_s, and Coulomb integrals of the hydrogen $1s$ with the p_π and p_σ electrons, K_π and K_σ in Stehn's notation. To solve the equations Stehn made the reasonable assumption that $K_\sigma = K_\pi = K_p$. Thus

$$\begin{aligned} K &= K_s + a_5 K_\pi + a_6 K_\sigma \\ &= K_s + Z_p K_p, \end{aligned} \tag{4}$$

where Z_p is the number of p electrons.

In view of the constancy of J_σ, the $2s^2-1s$ exchange K_s should also remain reasonably constant (as contrasted with the variation in K), and should be equal to the dissociation energy of BeH, which has no p electrons. The difference $K_p=(K-K_s)/Z_p$ is calculated and plotted on Fig. 1. This, then, is the Coulomb energy (other than the attraction $-e^2/r_e$ of each electron to the other nucleus, which is canceled by the nuclear repulsion term in the energy expression) of the hydrogen $1s$ and a $2p$ electron. As the series approaches more to a united atom K_p falls off to a small value of 0.2 ev, of the right order of magnitude for an atomic electrostatic repulsion of two $2p$ electrons.

FIG. 3. The linear dependence of $1/(r_e-0.34)$ on the atomic number Z, and the effective nuclear charge Z^*. For most excited states the internuclear distance is the same as in the ground state.

[8] N. Rosen, Phys. Rev. **38**, 2009 (1931).
[9] Slater and Frank, *Introduction to Theoretical Physics*, p. 432.

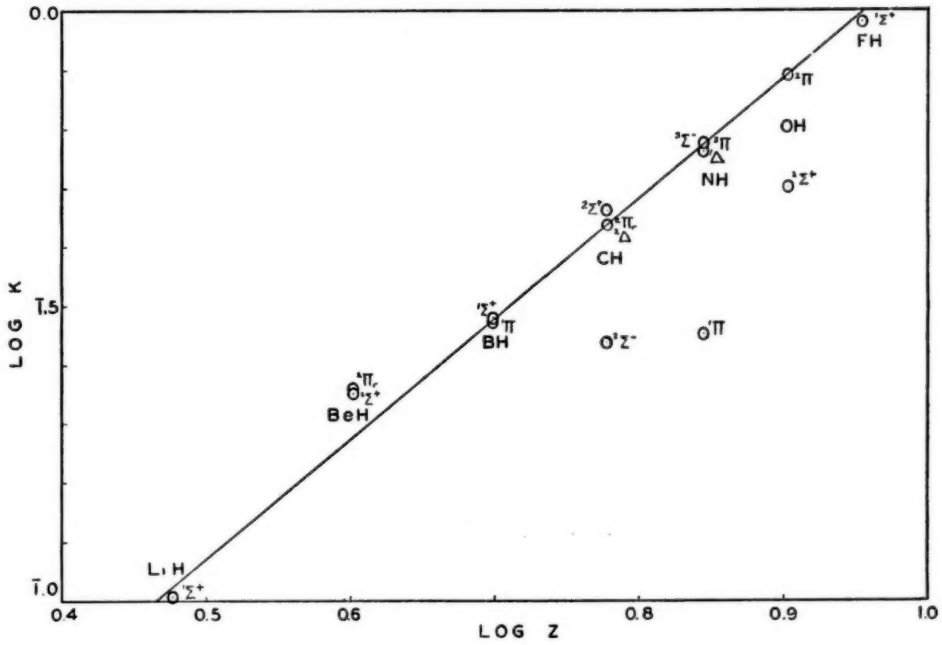

FIG. 4. Force-constant as a function of the atomic number, showing the invariance to electronic excitation.

BOND STRUCTURE

These results can be supplemented with the following facts (see Figs. 3 and 4, and Table I):

(1) the internuclear distance, r_e, and
(2) the force-constant, k, are smooth, but rapidly varying functions of Z (including BeH which has no p electrons), but
(3) and (4) are practically the same in the excited states of any one molecule.

On the other hand the integrals J_π and J_σ representing exchange of the hydrogen 1s electron with p_π or p_σ electrons of the heavy atom are much less dependent on Z, and of course do not always appear in the energy expressions (for the coefficients a_3 and a_4 in Eq. (1) are far from being smooth functions of Z).

Apparently, then, the exchange integrals with the p electrons do not determine r_e or k to any significant extent, which is especially surprising in the case of the σ electrons inasmuch as the σ integral contributes most to the energy.[10] It is to be concluded that the equilibrium distance and force-constant are predominantly determined by exchange with 2s electrons, and that the exchange energy with p_σ, although large, has a flat minimum, as is indeed the case as shown by evaluation of Rosen's expression for this integral.

Relative effect of different components of a potential curve

An integral that gives a large contribution to the stabilization energy does not necessarily affect r_e or k very much, for it may be flat. This phenomenon was emphasized by Pauling[11] in the case of the carbon-carbon bond distance. Even a small introduction of double or triple bond character shortens single bonds, whereas a similar amount of single bond wave function does not affect (i.e., lengthen) double or triple bonds. For consider a molecular potential curve that is made up of a linear combination, with coefficients x_i of component molecular orbital potential curves of different curvatures (i.e., force-constants) k_i, each with its own minimum at r_i,

$$V=\Sigma_i x_i k_i (r_i-r)^2. \tag{5}$$

The equilibrium distance is the weighted mean

$$r_e=\Sigma_i x_i k_i r_i/\Sigma_i x_i r_i \tag{6}$$

with weight factors k_i. That is, the most curved components contribute the most. A potential curve resulting from the usual type of exchange integral will have a curvature k_i roughly proportional to $1/r_i^2$. Hence a curve

[10] Since K is the sum of the Coulomb forces (positive) and exchange with $2s^2$, the latter will be somewhat larger than K, in fact equal to K_s, and be equal or larger than J_σ.

[11] Linus Pauling, Princeton lectures, 1938.

with a minimum relatively far out, as our J's, will not affect appreciably the r_e of the whole molecule.

The force-constant of the molecule is given by the second differential of (1), *viz.*,

$$k = a_2K'' + a_3J_\pi'' + a_4J_\sigma''. \quad (7)$$

Spectroscopic data show k is independent of a_3 and a_4, so the quantities J_π'' and J_σ'' must be small relative to K''; that is, the energy curves for exchange with p electrons are relatively flat.

Relations Between Internuclear Distance, Force-Constant and Nuclear Charge

With this picture of strong $1s-2s^2$ bonding it is possible to derive laws relating r_e, k and Z by a simple theory of the dependence of the dimensions of the $2s^2$ orbits on Z. These relations are smooth functions, which fit the data (including the excited states) very well for the series F, O, N, C, B, BeH. The values for LiH show a discontinuity, as is to be expected at the transition from the configuration $2s^2$ to $2s$. But there is no discontinuity apparent on the change of number of p electrons, either π or σ. These electrons have an effect only through shielding.

If then, the potential curve has a component in the form of $2s^2-1s$ exchange which predominates because of a sharp minimum at the short-

Table I.

Mol	Z	State	Config.	Energy	D_e	ν_{mol}	ν_{atom}	r_eA	ω_e cm^{-1}	Refs.
LiH	3	$X^1\Sigma^+$	—	—	2.47	0	0	1.593	1405.65	19
		$^1\Sigma^+$	—	—				2.600	234.41	
BeH	4	$^2\Sigma^+$	—	$^1S+K_s$	2.22	0	0	1.340	2058.5	8
		$^2\Pi$	—	—				1.330	2087.6	
BH	5	$A^1\Sigma^+$	σ	$^2P+K_\sigma+J_\sigma$	3.60	0	0	1.225	2366	2, 3
		$D^3\Pi$	π	$^2P+K_\pi-J_\pi$			0	1.198		3, 4
		$C^1\Pi$	π	$^2P+K_\pi+J_\pi$	0.73	2.847	0	1.219	2344	2, 3
		$B^3\Sigma^+$	σ	$^2P+K_\sigma-J_\sigma$			0	1.220		3, 4
CH	6	$X^2\Pi_r$	$\pi\sigma$	$^3P+\frac{3}{2}F_2+K_\pi+K_\sigma-\frac{1}{2}J_\pi+J_\sigma$	3.602	0	0	1.12	2824	5, 6
		$A^2\Delta$	π_+^2	$^1D+2K_\pi-J_\pi$		2.860	1.25	1.11	2800	8
		$B^2\Sigma^-$	$\pi_+\pi_-$	$^3P+2K_\pi+J_\pi$	0.39	3.175	0	1.094	2242	5, 6
		$C^2\Sigma^+$	$\pi_+\pi_-$	$^1D+6F_2+2K_\pi-J_\pi$		3.928	1.25	1.12	2906	8
NH	7	$X^3\Sigma^-$	$\pi_+\pi_-\sigma$	$^4S+3F_2+2K_\pi+K_\sigma-J_\pi+J_\sigma$	—	0	0	1.035	~3300	9, 10, 11
								1.045		13
		$a^1\Delta$	$\pi_+^2\sigma$	$^2D+2K_\pi+K_\sigma-J_\pi+J_\sigma$	—	a	2.37	1.041	3060	13, 14
								1.12	3183	12
		$b^1\Sigma^+$	$\pi_+\pi_-\sigma$	$^2P+2K_\pi+K_\sigma-J_\pi+J_\sigma$	—	$1.058+a$	0	1.043		13
		$A^3\Pi$	$\pi_+^2\pi_-$	$^2D+3F_2+3K_\pi-2J_\pi$		3.670	2.37	1.034	~3300	9, 10, 11
								1.046		13
		$C^1\Pi$	$\pi_+^2\pi_-$	$^2D+3F_2+3K_\pi$	—	$3.79+a$	2.37	1.123	2270	13, 14
								1.122		13, 14
OH	8	$A^2\Pi_i$	$\pi_+^2\pi_-\sigma$	$^3P+\frac{3}{2}F_2+3K_\pi+K_\sigma-\frac{3}{2}J_\pi+J_\sigma$	4.35	0	0	.964	3735	15, 16
								.974		17, 18
		$B^2\Sigma^+$	$\pi_+^2\pi_-^2$	$^1D+3F_2+4K_\pi$	2.26	4.03	1.94	1.009	3184	8
								1.015		17, 18
FH	9	$^1\Sigma^+$	$\pi_+^2\pi_-\sigma$	$^2P+4K_\pi+K_\sigma-2J_\pi+J_\sigma$	6.35	0	0	.864	4037	8
									4141	20

1. J. R. Stehn, J. Chem. Phys. **5**, 186 (1937).
2. S. F. Thunberg, Zeits. f. Physik **100**, 471 (1936).
3. G. M. Almy and R. B. Horsfall, Phys. Rev. **51**, 491 (1937).
4. W. Lochte-Holtgreven, and E. S. van der Vleugel, Zeits. f. Physik **70**, 188 (1931).
5. Shidei, Japanese J. Phys. **11**, 23 (1936).
6. A. McKellar and C. A. Bradley, Phys. Rev. **47**, 787 (1935).
7. Fagerholm, Naturwiss. **25**, 106 (1937).
8. H. Sponer, *Molekulspektren*, (1935).
9. G. W. Funke, Dissertation, Stockholm (1937).
10. G. W. Funke, Zeits. f. Physik **96**, 787 (1935).
11. G. W. Funke, Zeits. f. Physik **101**, 104 (1936).
12. Nakmara, Japanese J. Phys. **10**, 5 (1935).
13. R. W. Lunt, R. W. B. Pearse and E. C. W. Smith, Proc. Roy. Soc. **155**, 173, (1936) et seq.
14. Hori, Zeits. f. Physik **59**, 101 (1929).
15. Landolt-Bornstein, *Tabellen*, Vol. 3, p. 2873.
16. Bichowski and Rossini, *Thermochemistry of Chemical Substances* (1937).
17. Tanaka, Proc. Phys. Math. Soc. Japan **15**, 195, 272 (1933) and **16**, 365 (1934).
18. M. Ishaq, Proc. Roy. Soc. **159**, 110 (1937).
19. F. H. Crawford and T. Jorgensen, Phys. Rev. **47**, 932 (1935).
20. D. E. Kirkpatrick and E. O. Salant, Phys. Rev. **48**, 945 (1935).

est r_e, the whole series Be to FH should have r_e and k of the same potential curve, variation being due solely to contraction with increasing Z.

Internuclear distance

It is well established from measurements of the interatomic distances and from the simple idea of maximum overlapping that the internuclear distance is roughly the sum of the atomic radii. For $2s^2-1s$ binding

$$r_e=(n^2/Z-S)+a. \tag{8}$$

Here S is the shielding constant for the heavy atom, and n^2 is a little more than 2^2 in the case of s electron binding.[12] The distance a can be taken either as the hydrogen radius, of 1 atomic unit, or as the position of the *maximum* of the $1s$ hydrogen wave function from the hydrogen nucleus, 0.34 atomic units.

Curve I of Fig. 3 is a plot of $1/(r_e-0.34)$ *versus* Z, showing linearity in agreement with (8).

Since the $2s$ interchange fixes r_e, S refers to the shielding of a $2s$ electron. It is equal to $A-BZ_p$, where A is the $1s^22s$ shielding, B the shielding constant for a $2p$ on a $2s$ electron, and Z_p is the number of $2p$ electrons. Thus

$$\frac{1}{r_e-a}=\frac{Z^*}{n^2}, \tag{9}$$

$$Z^*=Z(1-BZ_p)-A. \tag{10}$$

For A the usual[9] 0.85 for each $1s$ electron, 0.35 for the other $2s$ electron were used. The constant B then plays the role of a parameter which is adjusted to make the graph of $1/(r_e-0.34)$ *versus* Z^* pass through the origin in accordance with (9). It turns out that the points still lie on a straight line, Fig. 3, with a slope of 4.28, which is a good value for n^2.

The required value of 0.77 for the shielding of p electrons (along the internuclear axis) is larger than the values found in the central fields of atoms. This is to be expected as p_σ electrons in cylindrical fields of molecules are well intermingled with the bonding electrons, and even p_π electrons have orbits located along the internuclear axis, not "dumbbells" at the end of the

[12] Reference 9, p. 445.

TABLE II.

Mol.	Z^*	$-J_\sigma$	$+J_\pi$	$-K$	$+K_p$	State	k megadynes/cm	k_{calc}	$Z^*\times(r_e-.34)$	kr_e^2/Z^{*2} ev	$k\times(r_e-.63)^2$
LiH	1.30	—	—	—	—	$X^1\Sigma^+$	0.102	0.037	4.284	4.80	0.203
						$^1\Sigma^+$	0.0311		4.247	3.88	.359
BeH	1.95	—	—	—	—	$^2\Sigma^+$	0.225	0.211	3.349	3.33	.228
						$^2\Pi_r$	0.231		5.957	3.37	.228
BH	2.18	2.34	0.52	1.26	0.98	$A^1\Sigma^+$	0.302	0.303	4.314	2.99	.213
						$D^1\Pi$			4.203		
						$C^1\Pi$	0.297		4.290	2.91	.207
						$B^1\Sigma^+$			4.292		
CH	2.41	2.27	0.80	1.21	0.50	$X^2\Pi_r$	0.434	0.438	4.290	2.94	.210
						$A^2\Delta$	0.426		4.244	2.84	.198
						$B^2\Sigma^-$	0.273		4.172	1.77	.119
						$C^2\Sigma^+$	0.459		4.290	3.12	.222
NH	2.64	2.20	0.90	(1.20)	0.34	$X^3\Sigma^+$	0.599	0.615	4.274	2.89	.205
									4.324	2.94	.222
						$a^1\Delta$	0.515		4.306	2.51	.181
						$b^1\Sigma^+$			4.313		
						$A^3\Pi$	0.599		4.269	2.85	.205
						$C^1\Pi$	0.283		4.710	1.61	.138
OH	2.87	2.13	0.92	1.27	0.24	$A^2\Pi_i$	0.774	0.838	4.261	2.75	.292
						$B^2\Sigma^+$	0.5622		4.506	2.19	.172
FH	3.10	2.06	0.93	2.43	~0	$^1\Sigma^+$	0.9601	1.10	4.018	2.34	.142

molecule. There is some indication that π electrons have a smaller shielding effect than the σ type.

This value of 0.77 for $2s-2p$ shielding is in agreement with the $2p-2p$ shielding of 0.63 obtained from our discussion of the exchange integral J_σ, and further, is the only one that fits the following equations for the force-constants.

Force-constants

From the theoretical calculations of the potential energy curves for H_2, H_2^+, HeH^+ and other studies of interatomic forces, it is seen that the attractive forces fall off as $-\exp(-ar)$, or as $-a'/r^6$, while repulsive forces have a range about the square of this, $\exp(-2ar)$ or b/r^{12}. Following Slater and Frank[12] we can estimate the constant a as Z^*/r_e, where Z^* is the effective nuclear charge for the principal binding electrons (10), giving a potential curve of the Morse type,

$$De^{-2Z^*(r-r_e)/r_e}-2De^{-Z^*(r-r_e)/r_e}. \tag{11}$$

The force-constant for this function is

$$k=(2Z^{*2}/r_e^2)D. \tag{12}$$

If it is true that $2s^2-1s$ exchange fixes k in the series BeH to FH, the D in (11) and (12) will be practically constant, and equal to K_s; therefore the quantity $kr_e^2/2Z^{*2}$ should be roughly constant, equal to K_s. Column (11) in Table II shows that the data are in fair agreement with this simple theory. The trend in K_s is almost the same as for J_σ; the average value is 2.94 ev, whereas the dissociation energy of BeH, also approximately equal to K_s is 2.22 ev.

Equations (9) and (12) can be combined to express the force-constant k as a function of Z^* alone,

$$k=\frac{2K_sZ^{*4}}{(n^2)^2+0.68(n^2)Z^*+0.12Z^{*2}}. \tag{13}$$

The best fit, column (9) of Table II, is with values of $K_s=2.94$ ev and $(n^2)=4.29$, values in excellent agreement with those obtained with the simpler formulae. At first sight this might be expected, but had there been a real trend from (9) and (12), the constants from (13) would not have been the same.

As a comparison, Badger's constant[13] is calculated in column (12), to show the agreement with the theoretical is as good as with the empirical formulae.

Summary

By the aid of Stehn's energy expressions we have made some analysis of the potential curves of the molecules BeH, BH, CH, NH, OH, FH. The force-constant and the internuclear distance are determined by $2s^2-1s$ exchange, and are not influenced by the p electrons. This accounts for their regular variation with Z, and invariance to electronic excitation. On the other hand this regularity is entirely dispersed in the case of the dissociation energies. That is, we cannot expect graphs of D *versus* Z, r_e or k to be simple curves, because in the formulae for D the p electrons contribute largely, in a fashion quite irregular with respect to Z, r_e or k, as displayed explicitly by Stehn's formulae.

The author takes pleasure in acknowledging the help of Professor J. H. Van Vleck and of Dr. J. R. Stehn in preparing this paper, and also the hospitality of the physics, chemistry and mathematics departments of Princeton University.

Appendix

Heat of dissociation of NH

There is no known value of the dissociation energy of NH. [The value of 102.2 kcal. quoted by Bichowski and Rossini[2] from Bates[14] is an upper limit.]

If we can rely on the smooth curves of Fig. 1 we can calculate, by means of Stehn's formulae, this dissociation energy as $D_e=3.61$ ev, or 83 cal. The thermal dissociation energy, D_0 will be $D_e-\frac{1}{2}\omega_e=79$ kcal.

Table III. *Bond energies of simple and saturated hydrides.*

CH	78.9 kcal.	$\frac{1}{4}$	CH_4	87.6 kcal.
NH	79 kcal.	$\frac{1}{3}$	NH_3	83.9 kcal.
OH	100.2 kcal.	$\frac{1}{2}$	OH_2	110.4 kcal.

This seems to be a good value in comparison with $\frac{1}{3}$ of the heat of formation of NH_3 from atoms, namely 84 kcal., a calculation suggested by the theory of directed valency. Table III is a summary of such a computation for CH, NH, and OH.

[13] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).

[14] Bates, Zeits. f. physik. Chemie, Bodenstein Festschrift, 329 (1931).

Dielectric Absorption in Polar Media and the Local Field

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The phenomena of dielectric dispersion and absorption in polar liquids subject to applied high frequency electrical fields are discussed on the basis of a modified Onsager theory for the local field. The results of this theory agree quite as well with experiment as do those from Debye's application of the hypothesis of hindered rotation with which the present work is compared. The application of the modified theory to the static case is also considered. A law of corresponding states is found to exist for the alcohols and an empirical equation proposed by Van Arkel and Snoek for "normal" polar liquids is shown to have an explanation in terms of the local field. The desirability of more complete measurements of dielectric constants and absorption as a function of temperature and frequency is stressed.

I. INTRODUCTION

THE familiar equations of Debye for the real and imaginary parts (ϵ', ϵ'') of the dielectric constant of a polar liquid in an alternating electric field $E=E_0 \exp(i\omega t)$ of frequency ν ($\nu=\omega/2\pi$) are

$$\epsilon'=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1+x^2),$$
$$\epsilon''=(\epsilon_0-\epsilon_\infty)x/(1+x^2). \quad (1)$$

Here ϵ_0 is the dielectric constant at zero frequency, due to the permanent moment plus induced polarization, and ϵ_∞ is the dielectric constant at infinite frequency due to the induced polarization only. The frequency dependent variable x is given by

$$x=(\epsilon_0+2)\omega\tau/(\epsilon_\infty+2), \quad (2)$$

where τ is the so-called relaxation time.

Equations (1) are derived on the assumption that the local field at a molecule can be represented by the Lorentz expression:

$$E_{\text{LOC}}=E+4\pi P/3=\tfrac{1}{3}(\epsilon+2)E. \quad (3)$$

It is further supposed that the orienting effect of this field on the molecule of dipole moment μ is opposed by a viscous force proportional to the angular velocity of rotation of the molecule. For spherical molecules of volume V in a liquid of viscosity η the parameter τ is then given by[1]

$$\tau=3\eta V/kT,$$

T being the absolute temperature.

[1] P. Debye, *Polar Molecules*, Chap. V.

The Clausius-Mossotti expression for ϵ may be written

$$\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}-\beta=0, \quad (4)$$

where $\beta=4\pi N\mu^2/9kT$ and N is the number of molecules per cc. It is well known that this expression, which is derived on assumption of the validity of (3), is not an adequate representation for polar media.[2] In particular, if induced polarization is neglected (4) predicts an infinite value of ϵ for $\beta=1$. Such values of β are found at temperatures of the order of room temperature or higher for substances with a large dipole moment but such a behavior of ϵ is, needless to say, not found experimentally. For nonstatic fields, Eqs. (1), although of the proper form to account for many of the observed facts, require in many cases unreasonable values of V in the parameter τ to give the characteristic frequency region of dispersion and absorption correctly, especially for liquids of high dielectric constants.

Debye and his co-workers have achieved considerable success in explaining these discrepancies by assuming that the dipole axis of a given molecule in a liquid is bound to an axis defined by the configuration of its neighbors by a "hindering" potential $-\mu F\cos\vartheta'$ where F is a potential energy and ϑ' the angle between the axes.[3]

Van Vleck [2] has, however, shown on the basis of statistical-mechanical calculations of dipole-

[2] J. H. Van Vleck, J. Chem. Phys. **5**, 556 (1937).
[3] P. Debye, Physik. Zeits. **36**, 193 (1935); P. Debye and W. Ramm, Ann. d. Physik **28**, 28 (1937).

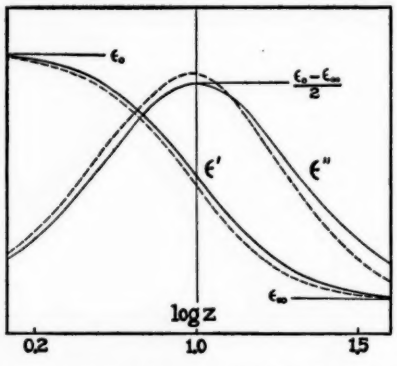

FIG. 1. Real and imaginary parts (ϵ', ϵ'') of the dielectric constant plotted against the frequency dependent variable z. Solid curves are for the approximate equations, dashed curves for the Onsager theory as explained in the text. The scale for ϵ'' is twice that for ϵ'.

dipole coupling that the local field as given by (3) is not an adequate representation of the state of affairs. Onsager [4] has obtained an expression for the local field on the view that the molecule in virtue of its electric moment has a modifying effect on the surrounding medium. This expression Van Vleck has shown to be in agreement with his results to a second approximation in the dipole-dipole coupling (the extent to which the calculations were carried). This agreement is, however, obtained only if one assumes in the dipole calculations that the molecules surrounding a given one may be represented as a continuous distribution. Van Vleck has also shown that the excessive saturation curvature of ϵ as a function of field strength found by using (3) is not predicted by the Onsager field. In view of all this it has seemed worthwhile to see what results are given by the Onsager theory as applied to the dielectric constant of polar liquids in radio-frequency fields.

II. Dispersion and Absorption for the Onsager Local Field

A. *Derivation.*—Onsager's formula may be written

$$\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}-\beta=(f-1)\beta, \tag{5}$$

where $f=3\epsilon(\epsilon_\infty+2)/(2\epsilon+\epsilon_\infty)(\epsilon+2)$. This formula is derived on the assumption of a continuous medium in which a given molecule occupies a spherical cavity. For a more realistic picture of the environment as a discrete assemblage agreement with Van Vleck's results can be obtained in an empirical way by multiplying the right side of (5) by a factor q ($0\leqslant q\leqslant 1$) as suggested by him in the paper referred to. Such a procedure can hardly be justified in any rigorous manner at the present time, but introduction of such a factor does not complicate matters unduly, and it is of interest to examine the behavior of the values of q required to obtain experimental agreement with (5) thus modified as will be done in Section III.

In Debye's analysis of the effect of a nonstatic field he shows that one obtains a complex factor multiplying the moment of the form $1/(1+i\omega\tau)$. Exactly the same considerations apply in the Onsager case and the net result is simply that the terms involving β are multiplied by $1/(1+i\omega\tau)$. The dielectric constant is then complex: $\epsilon=\epsilon'-i\epsilon''$. As it stands (5) is quadratic in ϵ and an exact solution is too unwieldy to be readily handled. However, if the quantity $3\epsilon/(2\epsilon+\epsilon_\infty)$ in f be replaced by $\frac{3}{2}$ the equation is linear in ϵ:

$$\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}-\beta=q\left[\frac{3(\epsilon_\infty+2)}{2(\epsilon+2)}-1\right]\beta, \tag{6}$$

and the essential difference between the Onsager and Lorentz fields is retained. Making this approximation, inserting the complex modifying factor and solving for ϵ', ϵ'', one finds:

$$\begin{aligned}\epsilon'&=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1+z^2),\\ \epsilon''&=(\epsilon_0-\epsilon_\infty)z/(1+z^2),\end{aligned} \tag{7}$$

where

$$\begin{aligned}z&=\omega\tau/(1-\delta),\\ \delta&=\tfrac{1}{3}\beta(\epsilon_\infty+2)(1-q).\end{aligned} \tag{8}$$

The curves for ϵ', ϵ'' are plotted against $\log z$ in Fig. 1 and for comparison the curves obtained by a rigorous solution of the Onsager equation with $\epsilon_0=10$, $\epsilon_\infty=2$ are indicated by dashed lines. The error in the approximate analysis is obviously not serious even for this small a value of ϵ_0.

B. *Comparison with experiment.*—It must be remembered that in applying the Debye Eqs. (1) the value of ϵ_0 is taken from the experimental data on the assumption that it satisfies the

[4] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

Clausius-Mossotti relation (4). This is, of course, not the case for polar substances, a fact which must be borne in mind when the results of the hypothesis of hindered rotation are compared with the present work. Since ϵ_0 does satisfy the modified Onsager Eqs. (6) derived on plausible assumptions, this latter relation is evidently preferable as a basis for consideration of dispersion and absorption.

Equations (7) are quite general expressions for ϵ', ϵ'' in that they contain the results of the Debye theory and the unmodified Onsager theory as special cases for $q=0$ and 1, respectively. The various cases are seen from Eqs. (7) and (8) to differ only in the form of the variable z defined in (8). From Fig. 1 the center of the region of dispersion and absorption occurs for $z=1$. Writing $\omega=\omega_{MAX}$ for this case one has from (8):

$$\begin{aligned} &\text{(a)}\quad (\epsilon_0+2)\omega_{MAX}\tau/(\epsilon_\infty+2)=1, \quad q=0, \quad \text{Debye},\\ &\text{(b)}\quad \omega_{MAX}\tau/(1-\delta)=1, \quad \text{Modified Onsager},\\ &\text{(c)}\quad \omega_{MAX}\tau=1, \quad q=1, \quad \text{Onsager}. \end{aligned} \tag{9}$$

Most liquids for which data on ϵ_0 over a wide temperature are available require values of q between 0.8 and 1.1 (see Section III) if Eq. (6) is to fit the facts. The corresponding values of δ do not depend markedly on the temperature and lie between 0.3 and -0.15. For the alcohols δ has values between 0.7 and 0.9 but the values of q are strongly temperature dependent as discussed in Section III. It is seen from these values of δ and the fact that $(\epsilon_0+2)/(\epsilon_\infty+2)$ is a large number that the values of τ found for a given ω_{MAX} from the Debye case (*a*) of (9) are considerably smaller than those required by (*b*) or (*c*). Experimentally, the values of τ for polar liquids found assuming the Debye theory are much too small for liquids of large static dielectric constant ϵ_0. That is, they require, on the assumption of viscous damping, values of the molecular volume V to which τ is then proportional, of a smaller order of magnitude than those inferred from independent data, e.g. the van der Waals volume for gases. The prediction of larger values of τ and hence V on the modified Onsager basis is thus in the right direction.

In general the experimental verification of (1) has consisted in seeing whether for a reasonable value of the molecular volume V, assuming η known, the data for ϵ', ϵ'' as a function of ω and T can be reproduced in their general behavior. It is unfortunate that almost the only nearly adequate data on dispersion and absorption of simple liquids are for the alcohols which are abnormal in their static dielectric properties and are otherwise known to be highly associated. Debye in his book finds very good agreement between the data of Mizushima on *n*-propyl alcohol for three different frequencies over a temperature range 20° to −60°C and calculated values of ϵ', ϵ'' from Eq. (1) using a value $V=34\times10^{-24}$ cm^3 (radius 2.0×10^{-8} cm). As good agreement can be obtained from (7) and (8) using the value $V=60\times10^{-24}$ cm^3 and the values of q required to give ϵ_0 correctly in (6) for the static case.

Schmelzer [5] has made absolute measurements of absorption for several alcohols at a single frequency and temperature and calculated the value of ω_{MAX} on the basis of an expression for ϵ'' as in (1) or (7). The values of V required on the basis of formulas (9) are given in Table I together with those deduced from the van der Waals equation of state.

A detailed agreement with other estimates of V is hardly to be expected when one considers the crudity of assuming viscous damping of spherical molecules but in view of how well such an hypothesis works for the problem of ionic mobilities one should expect a reasonable degree of correlation with values of V found in other ways. It is seen that the derivation with the modified local field does lead to quite reasonable estimates.

C. *Comparison with the hypothesis of hindered rotation.*—Debye and Ramm [3] in their paper on the effect of hindered rotation consider three

TABLE I. *Molecular volumes from the various assumptions about the local field and from the van der Waals coefficient (all $\times 10^{-24}$ cc).*

SUBSTANCE	DEBYE	MODIFIED ONSAGER	ONSAGER	VAN DER WAALS
Water	$V=0.5$	4.1	12	13
Methyl Alcohol	16	38	132	28
Ethyl Alcohol	16	30	111	35
n-Propyl Alcohol	40	49	227	42
Butyl Alcohol	72	76	350	47

[5] W. Schmelzer, Ann. d. Physik **28**, 35 (1937).

cases:

(a) The hindering energy $F \ll kT$,
(b) The hindering energy F is comparable with kT,
(c) The hindering energy $F \gg kT$.

The effect in case (a) is to replace the quantity $1/(1+i\omega\tau)$ multiplying β by a series of terms of the form:

$$1/(1+i\omega\tau/\lambda_n), \qquad (10)$$

where the λ_n are constants. These reduce for ω small to

$$[(1-y^2/9)-i\omega\tau(1-11y^2/54)],$$

where $y=F/kT$. The absorption is thus apparently reduced by the factor $(1-11y^2/54)$. However, y is to be so taken that the difference between ϵ_0 and ϵ_∞ is represented by $(1-y^2/9)\beta$ when one uses the correct value of the dipole moment μ in β rather than a spurious one. (The latter is implicitly done if one accepts the Clausius-Mossotti Eq. (4) as an expression for ϵ_0.) The absorption equations are written in terms of $\epsilon_0-\epsilon_\infty$ rather than β (Cf. Eqs. (1) and (7).) Hence the absorption written in this way is reduced by a factor $(1-11y^2/54)/(1-y^2/9)$ which has obviously much less effect than the factor one might at first expect to be correct.

From the series of terms in (10) one should expect a series of absorption regions and as a result a composite absorption curve somewhat broader, displaced to higher frequencies and with a slightly smaller maximum. This type of absorption is actually found for many *complex* substances but the curve is still much broader in most cases than such a series of terms seems capable of accounting for and in addition is in many cases symmetrical about the maximum on a logarithmic scale of frequency. It is difficult to see how this latter behavior can be given by terms of the form (10) with the constants λ_n varying in a reasonable way. There seems to be no evidence that the maximum of absorption is less or the frequency spread greater for *simple* liquids where we can have the greatest hope for the adequacy of either picture. If the region of dispersion and absorption is merely shifted on a frequency scale as compared to the prediction of the original Debye theory with a reasonable value of τ the explanation proposed here would seem to be superior.

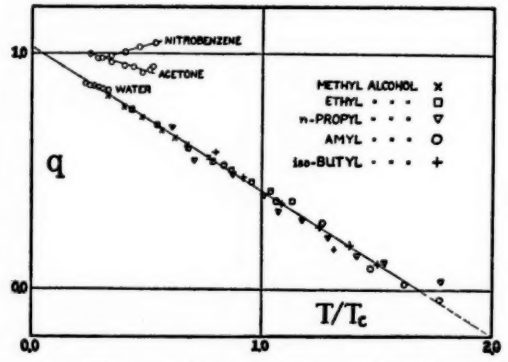

FIG. 2. The local field parameter q for the alcohols and water at different temperatures plotted against T/T_c $(=9kT/4\pi N\mu^2)$.

The foregoing remarks apply only if the hindering energy F is small compared with kT. For many polar liquids much larger values of F are necessary to compensate for the inadequacy of the Clausius-Mossotti formula. Unfortunately, in the intermediate case that F is comparable with kT the series development of Debye and Ramm breaks down and no definite conclusions can be drawn.

If $F \gg kT$ the effect of temperature is small compared with that of F. Debye and Ramm show that in this case kT is replaced by $F/2$ where it appears in β and τ. F is again to be so taken that this modified β gives ϵ_0 correctly in Eq. (4) with the true value of the moment μ. The maximum value of the absorption is the same as that given by the original equation with the experimental value of ϵ_0; the only difference is that there is now a justification for using this value. However the absorption has a different frequency dependence because of the new significance of τ. In particular a given value of the frequency of maximum absorption and hence τ requires a larger value of the molecular volume V if τ is given by $3\eta V/(F/2)$ rather than $3\eta V/kT$. This is, as already discussed, in the right direction. If one computes V for strongly polar liquids with an appropriate F the values are found to be comparable with those obtained on the modified Onsager hypothesis but in general slightly smaller. The latter is thus quite as satisfactory in the way of quantitative agreement and in addition there is no need to account for a large hindering potential F.

The inadequacy of the experimental data for simple polar liquids makes a more detailed discus-

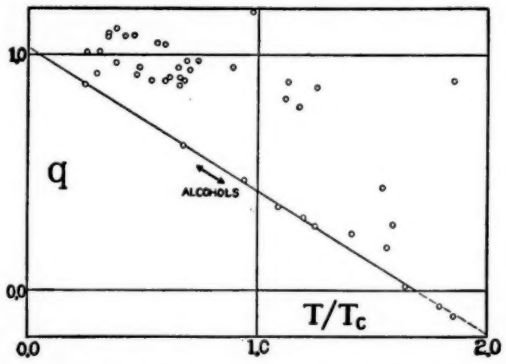

FIG. 3. The local field parameter q as computed from Wyman's data at room temperatures plotted against T/T_c.

sion hardly worthwhile at present. Enough has been said to show that the Onsager hypothesis leads to results which have the right trend from the original Debye theory and seems to work quite as well as Debye's hypothesis of hindered rotation. This lends additional confirmation to the view that a great deal of the difficulties with Eqs. (1) and (4) is due to the failure of Eq. (3) for the local field in polar media. A survey of the experimental data emphasizes the necessity for measurements over as wide a frequency and temperature range as possible, detailed consideration of isolated data being comparatively useless as the above discussion makes evident.

In the case of solids the interpretation of the relaxation time in terms of an ordinary viscosity is obviously impossible. One is then forced to introduce the relaxation virtually as an empirical parameter in the absence of a reasonable theory and there is therefore no such criterion for reasonableness of values found for τ as exists in the case of liquids.

III. The Local Field in the Static Case

A. *The temperature dependance of q.*—It remains to consider briefly the values of the parameter q required to give agreement of (6) with experimental results. A value $q=0$ corresponds to the Lorentz local field and $q=1$ to the Onsager case. Intermediate values might be expected to simulate a local field of the Onsager type for discrete molecular configurations. In the case of cubic structures, agreement with the calculations of Van Vleck requires $q\approx\frac{1}{2}$.

One can hardly attach too much significance to detailed behavior of the factor for specific cases but its general behavior should be of interest in indicating the extent to which dielectric constants of liquids can be explained in terms of dipole-dipole coupling. The significant parameter in such considerations is the temperature ($\beta=4\pi N\mu^2/9kT$) and unfortunately there are comparatively little data for dielectric constants of polar liquids over a wide range of temperature. Perhaps the most complete data exist for various alcohols and water which are known to the chemist as highly associated and hence are not ideally suited for the present purpose. One might expect q to be more or less independent of T, its value to be between $\frac{1}{2}$ and 1. Actually q is for these substances strongly temperature-dependent. However, as pointed out to the writer by Professor Van Vleck, one should expect a law of corresponding states if dipole-dipole coupling is the important factor. That is, the values of q as a function of a reduced temperature T/T_c should all lie on the same curve. Here T_c is the "Curie" temperature, having the value $4\pi N\mu^2/9k$ if induced polarization is neglected.[2] How well such a condition holds for water and the alcohols is seen in Fig. 2. This rather striking behavior suggests the possibility of a gradual transition from coupling of the dipoles to the free rotation of Debye's original theory as the temperature increases. However, it is unwise to generalize too much on the basis of data for such a limited number of abnormal substances and in addition it should be remembered that the dipole moment μ is very nearly the same for all these liquids, being due primarily to the OH group. The behavior for acetone and nitrobenzene, also plotted in Fig. 2, serves further to emphasize this need for caution. These comprise the substances for which the *International Critical Tables* give fairly complete temperature data.

B. *The data of Wyman.*—Wyman [6] has collected an extensive set of data on electric polarizabilities at room temperatures and dipole moments from which it is possible to compute q. Such values have been calculated for various related chemical series in his table for which the data seem reasonably reliable and they have been plotted against T/T_c in Fig. 3, which thus

[6] J. Wyman, Jr., J. Am. Chem. Soc. **58**, 1482 (1936).

shows that the required values are in general not at all unreasonable on the Onsager picture. It would be highly desirable to have more complete data on the dielectric constants of polar liquids as a function of temperature to see whether such a behavior as indicated by Fig. 2 for the alcohols holds for other series of related substances. Such data should be very valuable in any attempt at understanding the electrical properties of polar liquids generally.

C. *The local field and the work of van Arkel and Snoek.*—Another line of evidence which lends confirmation to the modified Onsager hypothesis in regard to the local field is found in a study by van Arkel and Snoek [7] of the experimental data for solutions of polar liquids in nonpolar solvents. They found that for a considerable number of "normal" polar liquids and over a wide range of concentrations the dielectric constant can be represented by a formula of the form:

$$\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}=\frac{4\pi N}{3}\cdot\frac{\mu^2}{3kT+(4\pi C/3)N\mu^2},$$

C being a constant characteristic of the polar liquid (N=number of polar molecules per cc) having values between 1 and 2. In the notation of the present work this may be written:

$$\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}=\frac{\beta}{1+C\beta}. \tag{11}$$

Now if one rewrites the modified Onsager formula (6) in terms of β on the right side, it assumes the form (taking ϵ_∞ to be the same for solute and solvent):

$$\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}=\frac{2+q}{2+q(\epsilon_\infty+2)\beta}\beta, \tag{12}$$

which is seen to be very similar to the expression (11). Namely, (12) differs from (11) only by having $2+q$ instead of 2 in the numerator on the right. Furthermore, the values of C found to work in (11) over a considerable range of concentration are such as to make the factor on the right agree quite well with the right side of (12) for most of the cases considered by these authors. Most of the data given are at one temperature or over only a limited range so the difference in functional dependence on β of the two expressions cannot be used to decide which of them is preferable. Here again it would be very desirable to have measurements at different concentrations made over as wide a temperature range as possible because of the dependence of β on T.

D. *Dielectric constants of solids.*—It should also be of interest to examine the values of q required to account for the dielectric properties of solids at various temperatures. There is, however, one thing to bear in mind: measurements of the dielectric constant as a function of T for solids have usually been made at a low frequency but one which is kept the same at all temperatures of measurement. Under such conditions many substances show a dielectric constant decreasing quite rapidly with T,[8] a behavior totally inexplicable in terms of the local field. However, it should be remembered that the relaxation times found experimentally for solids are very long as compared to those for liquids and may be expected to become increasingly so at lower temperatures. Thus the characteristic region of dispersion of the dielectric constant and absorption occurs at lower and lower frequencies and the dielectric constants found experimentally as above may be very far from the static dielectric constants at low temperatures, particularly if this region of dispersion is much broader than that predicted by the simple theories. Because of this difficulty and the incompleteness of dispersion and absorption measurements as a function of frequency no attempt has been made in the present work to carry out an analysis of the data for solids. It would be highly interesting to see how much of the apparent decrease is real and how much is due to the relaxation time by means of dispersion and absorption measurements over a wide frequency range.

IV. Conclusion

From the considerations above it appears reasonable to conclude that the difficulties found in attempts to apply the Clausius-Mossotti equation and the Debye equations for dispersion and absorption to measurements on dielectric media

[7] A. E. v. Arkel and J. L. Snoek, Trans. Faraday Soc. **30**, 707 (1934).

[8] See, for instance: R. H. Fowler, *Statistical Mechanics*, 2nd Ed., p. 824.

can be traced in large part to inadequacy of the Lorentz expression (3) for the local field. The hypothesis of hindered rotation then seems much less convincing as an explanation of the general behavior of such substances unless one considers it as an expression of the dipole-dipole coupling in the fashion that the Onsager local field appears to be. This latter with the modifying factor q is seen from several points of view to be a very satisfactory representation of the general behavior of dielectrics when one considers the crudeness of some of its basic assumptions. Because of the importance of temperature and frequency as parameters affecting the electrical properties of polar substances it would seem best to make a more detailed, critical study only when measurements are available over a wide range of these quantities for a reasonable number of different substances.

The writer is indebted to Professor J. H. Van Vleck, who suggested the problem, for his interest and helpful advice.

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Theory of the Viscosity of Unimolecular Films

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The equation for the fluidity of a liquid based on the reaction rate theory of viscous flow is modified to interpret the viscosity data for liquid films. The free energy of activation for viscous flow in the surface films, as calculated from the viscosity data of Harkins and Meyers, and Langmuir and Schafer, is found to be about twice that for flow in the liquid in bulk. This may be explained by the occurrence of various types of association in the liquid films, e.g. lateral association of the surface molecules with one another and vertical association with the solvent (solvation of the polar groups). Equations are given for the pressure and temperature effect on surface viscosity. It is shown how the knowledge of these effects may be used to interpret the structure of the films, and to separate and evaluate the contributions to the free energy of activation due to lateral association, solvation and hydrogen bonds.

THE general equation for the fluidity of a liquid has been formulated as follows:[1]

$$\phi=\frac{\Delta V}{f\lambda_1}=\frac{kT}{h}\cdot\frac{\lambda}{f\lambda_1}\left\{\exp\left(\frac{-\Delta F^{\ddagger}+(\lambda_2\lambda_3\lambda/2)f}{kT}\right)-\exp\left(\frac{-\Delta F^{\ddagger}-(\lambda_2\lambda_3\lambda/2)f}{kT}\right)\right\} \quad (1)$$

λ = distance between equilibrium positions in direction of flow,
λ_1 = perpendicular distance between adjacent molecules in direction of flow,
λ_2 = distance between adjacent molecules in direction of flow,
λ_3 = distance between molecules in plane of flow and normal to direction of flow,
f = applied external force per square centimeter,
ΔV = relative velocity of adjacent layers a distance λ_1 apart,
$\Delta F^{\ddagger}$ = free energy of activation for viscous flow per molecule.

Recently, Harkins and Meyers,[2] and Langmuir and Schafer [3] have determined the absolute viscosities of films of the liquid type. Whatever the mechanism for viscous flow in the surface layer, it can be treated by the same general reaction rate theory, since it is a process involving an activation energy. The three-dimensional equation may thus be easily modified to interpret these new data.

[1] Eyring, J. Chem. Phys. **4**, 283 (1936). Eyring and Ewell, ibid. **5**, 726 (1937).

[2] Harkins and Meyers, J. Chem. Phys. **5**, 601 (1937); **6**, 53 (1938).

[3] Langmuir and Schafer, J. Am. Chem. Soc. **59**, 2400 (1937).

TABLE I.

COMPOUND	$\Delta F\ddagger$ FOR LIQUID FILMS	$\Delta F\ddagger$ FOR PURE LIQUIDS	$\Delta F\ddagger$ (FILM)/ $\Delta F\ddagger$ (LIQ.)
Myristic acid	10360 cal.[2]	5770@70°C	1.80
Palmitic acid	10900[2]	5920 " "	1.84
Stearic acid	11030[2]	6300 " "	1.75
Oleic acid	10360[2]	6220@20°C	1.67
Cetyl alcohol	15300[3]	5800@60°C	2.62

The shear force acting on a single molecule at the interface is $f\lambda_2$ and it acts through a distance $\lambda/2$. Thus in the two-dimensional case

$$\Delta V=\lambda\frac{kT}{h}\left\{\exp\left(\frac{-\Delta F\ddagger+(\lambda/2)\lambda_2 f}{kT}\right)-\exp\left(\frac{-\Delta F\ddagger-(\lambda/2)\lambda_2 f}{kT}\right)\right\}. \quad (2)$$

Therefore the fluidity

$$\phi=\frac{\lambda kT}{\lambda_1 fh}e^{-\Delta F\ddagger/kT}\left\{\exp\left(\frac{\lambda f\lambda_2}{2kT}\right)-\exp\left(\frac{-\lambda f\lambda_2}{2kT}\right)\right\}.$$

This, on expansion, when $\lambda f\lambda_2 \ll kT$, becomes

$$\phi=\frac{\lambda\lambda\lambda_2}{\lambda_1 h}e^{-\Delta F\ddagger/kT}$$

To a first approximation $\lambda_1=\lambda$, and

$$\phi=(a/h)e^{-\Delta F\ddagger/kT} \quad (3)$$

where a is the cross-sectional area of the units which flow. Although the correctness of our general equations (2) and (3) does not depend on the exact mechanism of flow, we may most easily interpret the viscosity of liquid films by assuming the same model as was used in the case of the three-dimensional liquid. Therefore we picture the molecules oriented at the surface as rolling around one another whenever there is a neighboring hole in the surface which permits this rotation.

Using the available viscosity data we have calculated $\Delta F\ddagger$ for the viscous flow of the liquid films, and compared the values with those for the pure liquids obtained from the three-dimensional equation and viscosity data available in the literature. We have assumed in the calculation that a is the cross section of a single molecule; doubling the value of a increases $\Delta F\ddagger$ by only about 300 cals. The results are given in Table I.

Langmuir and Schafer found that the surface viscosities showed large variations with the age of the water on which the films were spread, the age of the film, the pH of the water, etc. With new water and newly spread monolayers, the surface viscosity of stearic acid was found to vary from 0.002 surface poises at pH 5.8 to 2.6, at pH 9.0. This corresponds to a variation in $\Delta F\ddagger$ from 12,100 cal. to 16,500 cal.

It is evident from these considerations that the free energy of activation for viscous flow in the surface layer is about two to three times that for flow in the liquid in bulk. In viscous flow, as in a chemical reaction, the process will go principally by the path requiring the least expenditure of free energy. Since the units of flow in the liquid are probably single molecules, there is evidently some degree of association in the liquid films. This may be due to lateral association of the surface molecules to give dimers, trimers, etc., or to vertical association or solvation of the polar groups. In either case the free energy of activation required for the flow process will be greater than it would be if the flow units were single molecules.

The widely varying viscosities found by Langmuir and Schafer suggest that no single explanation will cover all the observed data. Thus the high values of $\Delta F\ddagger$ may be due to a combination of such factors as vertical association, lateral association, and salt formation. The picture is akin to the situation in reaction kinetics in a system where there are a great many possible simultaneous reactions, with widely different reaction rates. The viscous flow process may be considered as a bimolecular reaction, consisting of the collision of a pair of molecules, rotation of the activated complex formed, and then dissociation of the complex.

If there are two different molecular species present, e.g. double molecules and single molecules, we may formulate the fluidity for the binary system as follows

$$\phi=\phi_1\frac{n_1^2}{n_{01}^2}+2\phi_{12}\frac{n_1n_2}{n_{01}n_{02}}+\phi_2\frac{n_2^2}{n_{02}^2}. \quad (4)$$

Here ϕ_1 is the specific fluidity for the rotation of

two single molecules, ϕ_{12}, for the rotation of a single around a double molecule, and ϕ_2, for the rotation of two double molecules; n_1 and n_2 are the number of molecules of each species per cc in the mixture, and n_{01} and n_{02} are the numbers per cc in a system containing only the one type of molecule. We see that the presence of large molecules will decrease the fluidity by cutting down the number of pairs of small molecules which are able to rotate. It is to be noted, however, that even if a large proportion of the surface molecules have such a large $\Delta F\ddagger$ as to be practically immobilized, the over-all fluidity, ϕ, may still be appreciable since it is the processes of low $\Delta F\ddagger$ that mainly determine the reaction rate. In other words ϕ_1 is much larger than ϕ_{12} or ϕ_2.

We may predict the pressure effect on viscosity as in the three-dimensional case. If δs is the area of the surface hole necessary for viscous flow, the free energy required to make a hole this size in the surface is $(p+p_i)\delta s$, per molecule. Here p is the applied external pressure; p_i is the internal pressure, defined as $(\partial E/\partial s)_T$ where s is the surface area; p and p_i are actually pressures per unit length per film thickness. Because film thickness cannot usually be varied arbitrarily, this dimension is customarily ignored in specifying surface forces and energies. If we put $N\delta s=\Sigma$, the free energy of making one mole of holes becomes $(p+p_i)\Sigma$.

We may now write

$$\Delta F\ddagger=RT\ln f+(p+p_i)\Sigma+\Delta F_s\ddagger. \qquad (5)$$

Here f is the partition function for the translational degree of freedom of the normal liquid which, in the activated state, is included in the factor kT/h. $RT\ln f$ amounts to about 1 kcal. for most substances. $\Delta F_s\ddagger$ is the structural free energy of activation. For nonpolar molecules it is negligible, but for systems having directional bonds, e.g. hydrogen bonds, the satisfactory saturation of these bonds in the activated state may be prevented because of their short range, directional nature.

It was shown in earlier treatments for liquids that p_iV ($V=Nv$, where v is volume of the hole required for flow process) was approximately one-third the energy required to vaporize the unit which flowed. Since the energy required to make a hole the size of a molecule equals the energy of vaporization, this was interpreted to mean that a hole one-third the size of the molecule is required for viscous flow. This picture then led automatically to an explanation of the pressure effect on viscosity. If we assume that $p_i\Sigma$ is one-third the energy required to vaporize the flow unit from the surface, we may apply this same treatment to the liquid films. Eq. (5) thus becomes

$$\Delta F\ddagger=RT\ln f+\Delta E_v/3+\Delta F_s\ddagger+p\Sigma. \qquad (6)$$

We might also use the well-known thermodynamic relationship $p+p_i=(\alpha/\beta)T$, where α and β are the coefficients of thermal expansion and compressibility of the liquid films, respectively. We then obtain from Eq. (5)

$$\Delta F\ddagger=RT\ln f+(\alpha/\beta)T\Sigma+\Delta F_s\ddagger. \qquad (7)$$

Eq. (7) suggests that if we knew the variation of α and β with temperature and pressure, we should have a method of predicting the temperature and pressure variation of the viscosity, provided that changes in $\Delta F_s\ddagger$ were negligible.

The only experimental measurement of the variation of surface viscosity with pressure is that of Talmud, Lubman, and Suchowolskata.[4] They found well defined maxima in the pressure *vs.* viscosity curves, which they attributed to a variation in the degree of hydration with pressure. Such a variation is likewise indicated by Langmuir's theory of the structure of liquid films. Since these authors gave no absolute viscosities, we were unable to calculate $\Delta F\ddagger$ from their data. We shall see below however that we can estimate the effect of hydration on $\Delta F\ddagger$, so that a further determination of the variation of viscosity with pressure might enable us to determine whether or not hydration varies with pressure.

A knowledge of the temperature coefficient of the surface viscosity would enable us to separate the entropy and energy terms in $\Delta F\ddagger$. This would furnish a method of investigating further the mechanism of the flow process. Any mechanism tending to decrease the number of molecules which flow readily would result in a decrease in the entropy of activation. A change in the type of molecule or of its interaction with the solvent would be evidenced by a change in the energy term.

[4] Talmud *et al.*, Zeits. f. physik. Chemie **A151**, 401 (1930).

Although we do not know the temperature variation of the surface viscosities we may roughly separate the entropy and energy terms by the following approximations. From the temperature coefficient of the viscosity of liquid stearic acid,[5] we find that at 70°C, $\Delta F\ddagger = 6300$ cal., $\Delta H\ddagger = 3580$ cal.; and $\Delta S\ddagger = 8$ e.u. It is probably safe to assume that the principal difference in the $\Delta F\ddagger$ terms in liquid in bulk and liquid film is in the terms for $\Delta H\ddagger$. Making this assumption we find that $\Delta H\ddagger$ for the film is 4830 cal. greater than for the fluid in bulk. This difference would be explained if each stearic acid molecule flowing in the surface had to drag with it one water molecule, since $\Delta H\ddagger$ for the viscous flow of water is about 4800 calories.[6]

Since the chief factor determining the viscosity of unimolecular films is $\Delta H\ddagger$, it is of interest to consider another method of estimating the contributions which make up this quantity. If the unit which flows is a single acid molecule with one or more solvent molecules attached, the energy required to make a hole can be written as the sum of two terms.

$$\Delta H\ddagger = \Delta H_1\ddagger + \Delta H_2\ddagger.$$

The term $\Delta H_1\ddagger$ is the energy required to make a hole in the fatty acid surface, while $\Delta H_2\ddagger$ is the energy required to extend the hole into the solvent. We expect $\Delta H_1\ddagger$ to be approximately one-third the heat of vaporization of a liquid film to a gaseous film. We have already seen that $\Delta H_2\ddagger$ can be estimated from either the viscosity or heat of vaporization of the solvent.

On the basis of his duplex film theory Langmuir found that the two-dimensional vapor pressure of films of myristic acid on dilute HCl obeyed the Clapeyron equation.[7] He gives the following equation, calculated from Adam's data:

$$\log_{10} p' = 8.058 - 1950/T.$$

From this we find that ΔE_{vap} of liquid to gaseous film = 8750 cal. Therefore $\Delta H_1\ddagger$ for myristic acid = 8750/3 or 2920 cal. Considering the approximations involved, this agrees reasonably with the 3580 cal. found for the energy of activation for viscous flow of stearic acid.

It should be emphasized that the gaseous film in equilibrium with a liquid film cannot be considered as analogous in all respects to a three-dimensional gas-liquid system. Since even for gaseous films there probably is some activation energy for viscous flow due to the solvated polar groups, we shall not, in general, have the situation in the real gas, where viscosity increases with temperature.

We have distinguished in the case of the liquid films two types of association: lateral association of the fatty acid molecules with themselves, and vertical association between the polar groups and the underlying water molecules. Thermodynamic consideration of the equation of state for the unimolecular films measures the lateral association. Kinetics provides a method of measuring both types of association. Thus a gaseous film will exhibit thermodynamic properties similar to those of a real gas. In regard to rate processes, such as viscosity and diffusion, the gaseous films will probably have the properties of a liquid.

We have outlined briefly the possible approaches to the viscosity data for liquid films on the basis of the reaction rate theory of viscous flow. As further data become available, the application of such methods should tell us more of the actual mechanisms involved, and of the actual structure of the surface layers.

We wish to acknowledge our indebtedness to Dr. Irving Langmuir and to Professor Hugh S. Taylor for helpful discussions on this subject.

[5] Bingham and Fornwalt, J. Rheology **1**, 372 (1930).
[6] Eyring and Ewell, reference 1, p. 733, Table 6.
[7] Langmuir, J. Chem. Phys. **1**, 770 (1933).

Electric Moments of the Methyl and Ethyl Alcohol Molecules

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The dielectric constant of methyl alcohol vapor has been measured at 14 temperatures between 25.0°C and 206.0°C. At each temperature measurements were made at an average of 23 different pressures ranging from zero to near saturation. The slope, obtained by least squares, of the resulting $(K-1)/(K+2)$ *versus* pressure curve gives one point on the Debye line. The 14 such points fall accurately on a straight line whose equation as obtained by least squares, and after making proper allowance for probable errors of calibration, is: $[(K-1)/(K+2)]RT/p' = (7.72\pm0.15)+(17{,}730\pm71)/T$. Using recently established values of the Boltzmann gas constant and Avogadro's number, this yields a value $(1.706\pm0.005)\times10^{-18}$ e.s.u. for the electric moment of the methyl alcohol molecule. Taking the sum of the electronic and atomic polarization as 8.6 leads to an electric moment of $(1.688\pm0.006)\times10^{-18}$. The mean $(1.698\pm0.005)\times10^{-18}$ is taken as the electric moment of the methyl alcohol molecule. Data on ethyl alcohol previously published by Knowles have been recalculated, using a least squares treatment throughout, and making a minor correction to the value used for the absolute zero of temperature. The data conform to the equation $[(K-1)/(K+2)]RT/p' = (13.06\pm0.20)+(17{,}725\pm87)/T$, wherein probable errors of calibration have again been allowed for. This yields a moment $(1.706\pm0.006)\times10^{-18}$. Taking the sum of electronic and atomic polarization as 13.6 leads to a moment $(1.696\pm0.008)\times10^{-18}$. The mean $(1.702\pm0.007)\times10^{-18}$ is taken as the electric moment of the ethyl alcohol molecule.

CONTINUING an earlier reported[1] effort to fix more definitely the values of the electric moment of several of the lighter alcohol molecules, the author has made extensive dielectric constant measurements on methyl alcohol vapor. Dielectric constants were measured by the heterodyne beat method, using apparatus previously described.[2] The vapor condenser with quartz insulators, and the vapor system, were the same as those used in previously reported work on water vapor[3] and isopropyl alcohol vapor.[1] Dielectric constants were measured at 14 different temperatures between 25.0°C and 206.0°C. At each temperature, measurements were made at an average of 23 different pressures, ranging from the lowest measurable up to near saturation when such saturated vapor pressure did not exceed one atmosphere. Two different samples of methyl alcohol were used, each of the highest purity obtainable and carefully dried.

Values of $(K-1)/(K+2)$ for a given temperature were plotted to a large scale against p', where p' represents the pressure the vapor would exert were it an ideal gas; the quantity p' is obtained from the observed pressure p and the van der Waals constants a and b, thus:

$$p' = p[1+(p/RT)(a/RT-b)].$$

At the higher temperatures, for which the highest pressures used were far below saturation, the resulting curves are accurately linear over their entire range. At lower temperatures, slight curvature is apparent at the higher pressures, though a large scale plot is necessary to detect it except very close to saturation. The only use made of such plots was to determine the extent of linearity. Barely perceptible curvature became apparent at pressures approximately two-thirds saturation. For each temperature the slope of the best least squares line through all points on the linear section was found; the average number of points on these linear sections was 19. The several advantages of securing extensive data and of the least square treatment of these data have been discussed previously.[1]

The molecular polarization is given by

$$(K-1)M/(K+2)d = (K-1)RT/(K+2)p' = A+B/T,$$

the last equality being a result of the Debye theory. The molecular polarization at each temperature was obtained from the slope of the $(K-1)/(K+2)$ *versus* p' curve for that temperature. The accuracy of the data can be judged from the calculated molecular polarizations and their probable errors as shown in Table I.

Figure 1 shows the products of molecular polarization and absolute temperature plotted

[1] Stranathan, J. Chem. Phys. **5**, 828 (1937).
[2] Stranathan, Rev. Sci. Inst. **5**, 315, 334 (1934).
[3] Stranathan, Phys. Rev. **48**, 538 (1935).

against T. The data fall accurately on a straight line, no point being off by more that 0.4 percent. Previous data by Miles[4] and by Kubo[5] are also shown. In calculating the best straight line through the 14 points of the present work, the question arises as to how the individual points should be weighted. While the author doubts that all variations are truly accidental, he feels that the largest are. Under such circumstances it appears advisable to weight each point inversely proportional to the square of its probable error. With such weighting, a least square solution for the best straight line through the author's data gives:

$$(K-1)RT/(K+2)p' = (7.72\pm0.15)+(17{,}730\pm59)/T.$$

Giving all points equal weights results in essentially the same equation, the constants so obtained being (7.55 ± 0.13) and $(17{,}797\pm52)$.

According to the Debye theory, the permanent electric moment u is given by:

$$u=(9kB/4\pi N)^{\frac{1}{2}},$$

where k is the Boltzmann gas constant per molecule and N is Avogadro's number. Recent work of Bearden,[6] Kellström,[7] and many others on a new value for the electronic charge leads to new values of N and k. These works have been so numerous and so convincing that there appears no reason for delaying longer the use of these new values in calculations of electric moments. Taking the gas constant per mole as $(8.3136\pm0.0010)\times10^{7}$ ergs per $C°$,[8] and N as $(6.0230\pm0.0005)\times10^{23}$ molecules per gram mole,[9] then $k=(1.3803\pm0.0002)\times10^{-16}$; hence,

$$u=(1.2811\pm0.0002)\times10^{-20}B^{\frac{1}{2}}.$$

This is larger than the value based upon constants previously accepted[8] by a factor 1.0069; hence all previous moments obtained from dielectric studies should be increased by this factor. While the difference is not great, it is definitely larger than the probable errors associated with a number of moments. The electric moment of the methyl alcohol molecule obtained from the present data is $(1.7058\pm0.0039)\times10^{-18}$ e.s.u.[10]

The probable errors quoted above are those calculated from accidental variations of observed data. Two other appreciable errors enter in the calibration of apparatus. Numerous and varied measurements of the effective capacity of the evacuated vapor condenser indicate that 1 part per 1000 would be a reasonable estimate of the probable error associated with this measurement. Similarly, an allowance of 2 parts per 1000 might be associated with the intercalibration of the large (1500 $\mu\mu f$) condenser used in measuring the effective capacity of the evacuated vapor condenser and the small (15 $\mu\mu f$) condenser used in measuring the increase in capacity occasioned by the presence of the vapor. Error introduced through measurement of temperature is negli-

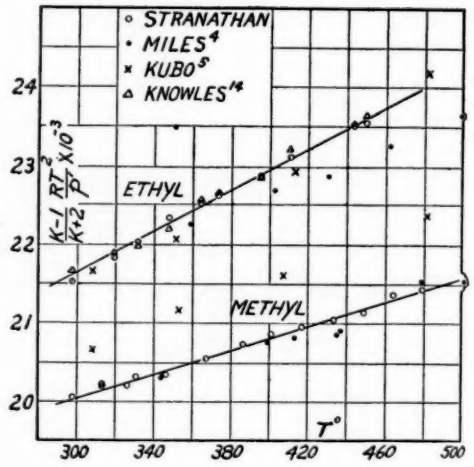

FIG. 1.

TABLE I. *Methyl alcohol. Experimental values of molecular polarization, with associated probable errors. Values of T are absolute temperatures in C°.*

TEMPERATURE T	MOLECULAR POLARIZATION	TEMPERATURE T	MOLECULAR POLARIZATION
298.2	67.29 ±0.25	386.5	53.633±0.073
313.7	64.39 ± .12	401.7	51.934± .063
313.7	64.47 ± .11	417.1	50.235± .037
326.6	61.86 ± .12	433.4	48.565± .035
331.2	61.32 ± .18	449.0	47.055± .039
346.7	58.684± .083	464.2	46.007± .029
367.4	55.927± .097	479.2	44.735± .030

[4] Miles, Phys. Rev. **34**, 964 (1929).
[5] Kubo, Inst. Phys. Chem. Res., Tokyo, Sci. Papers **26**, 242 (1935).
[6] Bearden, Phys. Rev. **48**, 385 (1935).
[7] Kellström, Nature **136**, 682 (1935); Phil. Mag. **23**, 313 (1937).
[8] Birge, Rev. Mod. Phys. **1**, 1 (1929).
[9] Birge, Nature **137**, 187 (1936).
[10] This moment was reported as 1.694×10^{-18} at the Indianapolis Meeting of the Am. Phys. Soc. (1937). When corrected to the new values of constants used here this corresponds exactly to the value here reported.

gible. Error due to adsorption of material on the insulator surfaces[3] may not be completely eliminated even by the procedure used here, though the residual must be small. Some evidence[11] indicates an appreciable error due to failure of the van der Waals gas law to represent accurately the density of the vapor in terms of its pressure. As far as is known, however, this error is quite small for measurements made at low pressures. If allowance is made for the probable errors of calibration, it is found

$$(K-1)RT/(K+2)p' = (7.72\pm0.15)+(17{,}730\pm71)/T$$

and $u=(1.7058\pm0.0048)\times10^{-18}$. The present results are compared with those of other extended works on vapors in Table II. While results of dilute solution studies are in general agreement with those on vapors, they are not as reliable; therefore they are not included.

The term A should be the sum of the electronic and atomic polarizations. A fair estimate[12] of this sum is a value 5 percent greater than the molecular refraction for the Na D line. Hence, one expects a constant term A about $(1.05\times8.23)=8.6$, whereas the experimental value found here is (7.72 ± 0.15). The difference may be experimental error, though it is considerably larger than one would suspect from the associated probable error. As Groves and Sugden[13] point out, it may be preferable in the calculation of moments to use the term A estimated from optical data. If A is taken as 8.6, then statistical weighting of data at different temperatures leads to a value $B=(17{,}354\pm11)$ and $u=(1.6877\pm0.0008)\times10^{-18}$. This appears much better determined, and the method is probably preferable for comparison of moments where calibration errors cancel out. However, if the same allowance as before is made for calibration errors, together with an allowance of 2 percent in the value chosen for A, we find $B=(17{,}354\pm80)$ and $u=(1.6877\pm0.0055)\times10^{-18}$. This moment is smaller than that found entirely from dielectric data by about twice the sum of the probable errors. The mean of these $(1.698\pm0.005)\times10^{-18}$, may be taken as the most probable value for the moment of the methyl alcohol molecule. Results of similar calculations from data of other workers are shown in Table II.

The data of Knowles[14] on ethyl alcohol vapor appears sufficiently extensive and reliable to warrant a least squares treatment. Knowles obtained data at 10 different temperatures between 24.55°C and 177.1°C. Observations at an average of 17 widely different pressures were made at each temperature. An average of 14 of these points fell on the straight line section of each curve. The author, having the original data available, has therefore made a recalculation, using least squares throughout, and making a minor correction for the previous use of the approximate value −273.0°C for the absolute zero of temperature. The resulting molecular polarizations with their associated probable errors are shown in Table III.

Products of molecular polarization and absolute temperature are shown plotted against absolute temperature in Fig. 1. The 10 points fall accurately on a straight line, no point being off by more than 0.4 percent. The previous points

TABLE II. *Comparison of results. A, B, and moments under (1) are calculated entirely from dielectric data. Moments under (2) are calculated by taking A = 8.6 for methyl alcohol and 13.6 for ethyl alcohol. All moments are on the basis of the new values of Avogadro's number and Boltzmann's gas constant.*

AUTHOR	A	B	$u\times10^{18}$ (1)	$u\times10^{18}$ (2)
Methyl Alcohol				
Stranathan	7.72±0.15	17,730±71	1.706±0.005	1.688±0.006
Miles[4]	8.13	17,430	1.691	1.684
Kubo[5]	9.54	17,710	1.705	1.724
Ethyl Alcohol				
Stranathan	13.06±0.20	17,725±87	1.706±0.006	1.696±0.008
Knowles[14]	13.6	17,550	1.698	1.697
Miles[4]	11.80	17,780	1.708	1.675
Kubo[5]	14.25	17,200	1.680	1.691

[11] Stuart, Zeits. f. Physik **51**, 490 (1928).
[12] Sugden, Trans. Faraday Soc. **30**, 738 (1934).
[13] Groves and Sugden, J. Chem. Soc. London, 158, Jan. (1937).

TABLE III. *Ethyl alcohol. Experimental values of molecular polarization, with associated probable errors. Values of T are absolute temperatures in C°.*

TEMPERATURE T	MOLECULAR POLARIZATION	TEMPERATURE T	MOLECULAR POLARIZATION
297.7	72.30±0.46	373.3	60.58±0.23
319.7	68.28± .34	395.5	57.84± .11
332.0	66.39± .11	410.9	56.29± .09
347.9	64.21± .17	443.6	53.02± .16
364.3	61.83± .34	450.2	52.33± .34

[14] Knowles, J. Phys. Chem. **36**, 2554 (1932).

obtained graphically by Knowles[14] from the same data, as well as previous data by Miles[4] and by Kubo[5] are shown. If the present points are weighted statistically, a least squares solution for the best straight line through them gives:

$$(K-1)RT/(K+2)p' = (13.06\pm0.20)+(17{,}725\pm78)/T.$$

This yields an electric moment $(1.7056\pm0.0052)\times10^{-18}$ for the ethyl alcohol molecule. Giving equal weights to all points leads to constants (13.35 ± 0.23) and $(17{,}610\pm85)$ in the above equation, thus yielding a moment $(1.7000\pm0.0058)\times10^{-18}$. The probable errors of calibration in Knowles work probably approximated those estimated in the present work on methyl alcohol. If the same allowance is made for them, we obtain from a statistical weighting of points:

$$(K-1)RT/(K+2)p' = (13.06\pm0.20)+(17{,}725\pm87)/T$$

from which $u=(1.7056\pm0.0059)\times10^{-18}$. These results are compared with other extended works on the vapor in Table II.

The constant term $A=(13.06\pm0.20)$ is again slightly smaller than the value $(1.05\times12.93)=13.6$ which we might reasonably expect. Taking $A=13.6$, statistical weighting of data at the various temperatures leads to values $B=(17{,}517\pm8)$ and $u=(1.6956\pm0.00055)\times10^{-18}$. If allowance is made for probable errors of calibration, together with a 2 percent probable error in the value chosen for A, then $B=(17{,}517\pm110)$ and $u=(1.6956\pm0.0076)\times10^{-18}$. This moment is smaller than that found entirely from dielectric data by somewhat less than the sum of the probable error. The mean $(1.702\pm0.007)\times10^{-18}$ may be taken as the most probable value for the moment of the ethyl alcohol molecule. Results of similar calculations from data of other workers are shown in Table II.

Judging from the general agreement of results of various workers, together with the probable errors associated with these, it appears that little real improvement can be made in the moments of the methyl and ethyl alcohol molecules until several possible sources of error are eliminated. The author is attempting several improvements in this direction before proceeding to a study of other moments.

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The Transference Numbers of Potassium Acetate in Aqueous Solution

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The transference numbers for aqueous solutions of potassium acetate at 25°C have been determined by the moving boundary method for the concentration range 0.01 N to 0.25 N. Two different types of cell and two different methods of measuring the number of coulombs were employed. Up to 0.16 N the transference numbers can be represented by the Shedlovsky-Longsworth equation within ±0.05 percent, and lead to a transference number for the cation at infinite dilution of 0.6428, in close agreement with that obtained from the limiting ionic mobilities.

IN recent years the determination of the transference numbers of ions in solution by the moving boundary method has been developed (thanks primarily to the work of MacInnes, Longsworth and their associates) until it will yield results of the highest precision; combined with accurate conductivity data, such numbers permit the calculation of limiting ionic mobilities with an accuracy of a part in several thousand. In the course of a study of the transference numbers for several electrolytes, Longsworth[1] has determined the transference numbers for solutions of sodium acetate; in this paper we report the numbers for solutions of potassium acetate.

[1] Longsworth, J. Am. Chem. Soc. **57**, 1185 (1935).

Since the moving boundary method has been adequately discussed in the literature,[2] no general description is needed here. The cells used were of two types; the first (referred to as I) is essentially that of Smith[3] and is similar to that used by Reevely and Gordon;[4] here a lithium acetate solution serves as indicator solution with a descending boundary. The electrode on the closed side (the cathode) was a platinum wire covered with fused silver chloride, and the general technique of filling the cell and forming the boundary was essentially theirs. In our measurements, the graduated tube (*A* in their Fig. 1) had an internal diameter of 4.3 mm. The second type (II) was a simplified autogenic boundary cell with rising boundary, illustrated in Fig. 1. The anode (of chemically pure cadmium) was carefully machined to fit the lower end of the graduated Pyrex tube, and before each experiment was sealed in the tube with De Khotinsky cement. To do this the lower end of the tube was heated by a small wire resistance bound around it, and the anode, whose sides had been covered with melted cement, was pressed into place; the lowest graduation on the tube is far enough from the heater so that there is no appreciable rise in temperature of the graduated part of the tube during the brief heating. The tube *B* was of sufficient length to ensure that none of the products of electrolysis at the cathode (a platinum wire covered with fused silver chloride) could reach the graduated tube during a run. In filling the cell, solution was added at *C*, any air that might be trapped in the graduated tube being allowed to escape through a narrow capillary inserted at *A*, the capillary being removed after filling. Two cells of type II were used (internal diameter of the graduated tube 3.4 and 2.5 mm). The volumes between graduations in all three cells were determined by mercury weighings as recommended by MacInnes, Cowperthwaite and Huang.[5] The cells were mounted in a glass-sided water bath, electrically controlled to ±0.01°C, and the movement of the boundary was followed by the illuminated slit method recommended by MacInnes and Longsworth.[2]

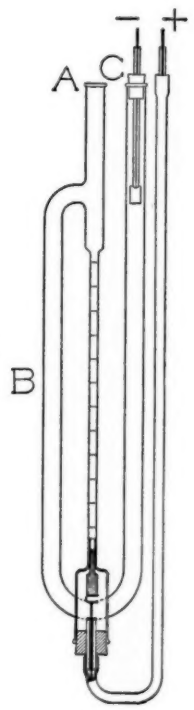

FIG. 1.

To determine the number of coulombs necessary to displace the boundary through a known volume, two entirely different methods of measurement were employed. The first of these involved the use of microcoulometers as described by Reevely and Gordon.[4] The cathodes were small platinum crucibles, and the anodes were silver wires surrounded by glass shields perforated at the sides to permit the passage of the current; each coulometer contained 5 cc of a 10 percent silver nitrate solution tested as recommended by Rosa and Vinal.[6] The only change in the technique from that of Reevely and Gordon was that the removal of the electrolyte and wash water from the crucible after the experiment was effected by suction using a small filter stick of a type familiar in microchemical work; the stick was always weighed with its coulometer, and thus there was no chance of loss of minute silver crystals. Duplicate determinations of the number of coulombs by this method as a rule are self-consistent to 0.03

[2] MacInnes and Longsworth, Chem. Rev. **11**, 171 (1932).
[3] Smith, Nat. Bur. Stand. J. Research **6**, 917 (1931).
[4] Reevely and Gordon, Trans. Electrochem. Soc. **26**, 261 (1933).
[5] MacInnes, Cowperthwaite and Huang, J. Am. Chem. Soc. **49**, 1710 (1927).
[6] Rosa and Vinal, Nat. Bur. Stand. Bull. **13**, 479 (1916).

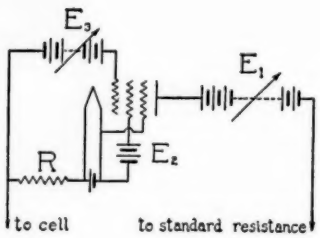

FIG. 2.

percent or better when the total weight of silver deposited is from 10 to 40 mg; numerous trials have shown that such determinations agree within the same limit of accuracy with the result of current-time measurements.

The second method is what might be called a semi-constant current device, which permits the number of coulombs to be measured from current time readings without employing the elaborate apparatus developed by MacInnes, Cowperthwaite and Blanchard.[7] The significant features are shown in Fig. 2; a somewhat similar circuit has been reported by Hartley and Donaldson.[8] The 1 *B* 4 vacuum tube has the characteristic that the plate current is almost independent of the plate voltage; consequently when the tube is connected as shown, the current is practically independent of the internal resistance of the cell, which may increase by as much as 100 percent during the course of a run. The potential E_1 is supplied by 45-volt B batteries, and the filament current by a 2-volt storage cell; for satisfactory operation E_1 can be varied up to 630 volts depending on the resistance to be expected in the cell. The screen voltage E_2 is kept at $62\frac{1}{2}$ volts, and the grid bias resistance R is about 20,000 ohms; small C batteries E_3 are used to bring the grid back to 2.5–4.0 volts negative. During an experiment, there is a slight but steady fall in current,[9] but this can be followed without difficulty by readings at 5- or 10-minute intervals; a simple graphical integration then gives the mean effective current during any part of the run. The current was measured by means of a 500-ohm certificated standard resistance and a Leeds and Northrup type K potentiometer, while time readings to the nearest half-second were effected by an electrical chronograph.

The potassium acetate solutions were made by essentially the method employed by MacInnes and Shedlovsky[10] in preparing their sodium acetate solutions. B.D.H. "analar" potassium bicarbonate, recrystallized from conductivity water, was heated in a platinum crucible to constant weight at 350°C in an atmosphere of CO_2; a weighed amount of the resulting normal carbonate was dissolved in water, a weighed quantity of glacial acetic acid, prepared after the method of Bousfield and Lowry,[11] was added in slight excess of the amount needed to neutralize the carbonate, the solution was boiled to remove CO_2, and then diluted gravimetrically to form a stock solution of convenient strength. All solutions were prepared by gravimetric dilution of such stock solutions. It was found essential to evacuate any solution before placing it in the cell, but weighings before and after evacuation

TABLE I.

CELL	C	t_+obs	SOL. CORR.	VOL. CORR.	t_+	t_+calc
II	0.009963	0.6493 .6499 .6478	0.0007	−0.0000	0.6497	0.6498
II	0.02184_0	.6525 .6529	0.0003	−0.0001	.6529	.6527
II	0.03631_7	.6557 .6548	0.0003	−0.0002	.6554	.6552
I	0.05003	.6569 .6565 .6574	0.0002	−0.0002	.6569	.6569
II	0.06627	.6592 .6588	0.0001	−0.0003	.6588	.6585
I	0.09990	.6613 .6605	0.0000	−0.0003	.6606	.6609
II	0.10747	.6618 .6614	0.0000	−0.0006	.6610	.6614
I	0.16964	.6643 .6647	0.0000	−0.0004	.6641	.6639
I	0.2521	.6690 .6696	0.0000	−0.0006	.6687	.6652

[7] MacInnes, Cowperthwaite and Blanchard, J. Am. Chem. Soc. **48**, 1909 (1926).

[8] Hartley and Donaldson, Trans. Faraday Soc. **33**, 457 (1937).

[9] For example, in one experiment with 0.06627 *N* solution, the current when the boundary crossed the first of the division marks was 1.4668 ma, while when it crossed the last, the current had fallen to 1.4639 ma.

[10] MacInnes and Shedlovsky, J. Am. Chem. Soc. **54**, 1429 (1932).

[11] Bousfield and Lowry, J. Chem. Soc. **99**, 1432 (1911).

measured any loss in water from this cause. The lithium acetate solutions, required for cell I, were made by the same procedure, the lithium carbonate being twice recrystallized from hot conductivity water. The conductivity water used had a specific conductivity of from 0.4 to 1.0×10^{-6}.

The *p*H of the acetate solutions was always adjusted to 5.5–5.8 (by the addition of weighed amounts of acetic acid after dilution if necessary)

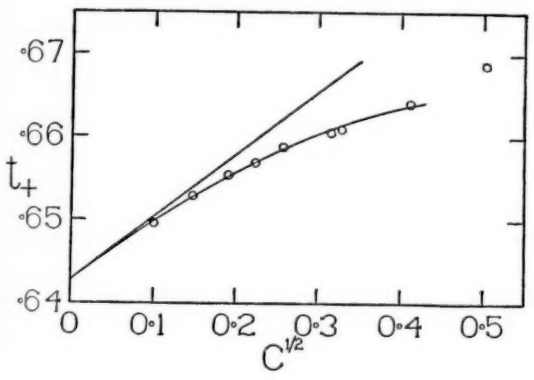

FIG. 3.

since by so doing the effect of dissolved carbon dioxide is minimized; the *p*H was determined colorimetrically with brom-cresol purple or by means of a quinhydrone electrode. The concentration of potassium acetate in the solution was calculated from its potassium content, and the effect of the slight excess of acetic acid was taken into account in computing the solvent correction; see below and also reference 10. In computing the volumetric concentration of the solutions from the gravimetric concentration, density data[12] from *International Critical Tables* were employed.

Table I summarizes the results; t_{+obs} is computed by the relation $t_{+obs}=1000VC/f$ where C is the concentration of the solution in equivalents per liter and f is the number of faradays necessary to displace the boundary through V cc. When f was measured by means of current time readings, the number recorded in the table is obtained by averaging the results of at least 6 independent measurements of the number of coulombs required to displace the boundary between two of the division marks on the

[12] *International Critical Tables*, Vol. 3, p. 90.

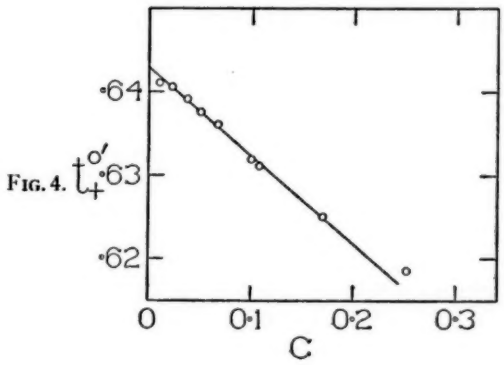

FIG. 4.

graduated tube; when f was measured by coulometer, the entry is the average of three independent measurements, each corresponding to the f obtained from one coulometer. In general, the values of t_{+obs} thus obtained from one experiment are self-consistent to 2 or 3 units in the fourth decimal place or better, although the variation from one experiment to the next is somewhat greater.

The numbers of column 3 are subject to two corrections. The first, the solvent correction, which must be added to t_{+obs}, has been shown[13] to be $t_+\cdot$ (conductivity of solvent)/(conductivity of solute). The conductivity of the solvent in our solutions is from two distinct causes, from the excess acetic acid added in making up the solution, and from residual impurities (apart from carbon dioxide) present in the conductivity water. We estimate the specific conductivity of the solvent due to this latter factor as 0.6×10^{-6}; the correction due to the former can be calculated from the measured hydrogen ion concentration of the solution by using the limiting mobilities listed by MacInnes, Shedlovsky and Longsworth[14] for the ions involved. The resulting solvent corrections for the various solutions are given in the fourth column of the table.

The second, or volume correction is given by

$$t_+=t_{+obs}\pm C\Delta V/1000$$

where ΔV is the change in volume in cc brought about at the electrode on the closed side by the passage of one faraday. The upper sign is

[13] For a general discussion of the solvent correction, see reference 2, and for the special case of an acetate solution containing free acetic acid, see reference 10.

[14] MacInnes, Shedlovsky and Longsworth, J. Am. Chem. Soc. **54**, 2758 (1932).

appropriate for cell I and the lower for cell II; ΔV is given by

$$\Delta V = V_{Ag} - V_{AgCl} + \bar{V}_{KCl} - t_- \cdot \bar{V}_{KAc}, \quad \text{(I)}$$

$$\Delta V = \tfrac{1}{2}\bar{V}_{CdAc_2} - \tfrac{1}{2}V_{Cd} - t_+ \cdot \bar{V}_{KAc}. \quad \text{(II)}$$

Here t_+ and t_- are the transference numbers of potassium and acetate ion, V_{Ag}, V_{AgCl} and V_{Cd} are the molal volumes of silver, silver chloride and cadmium, and $\bar{V}_{KCl}$, $\bar{V}_{KAc}$ and $\bar{V}_{CdAc_2}$ are the partial molal volumes of potassium chloride, potassium acetate and cadmium acetate, respectively; from the numerical values of these quantities listed by Longsworth,[1] the volume corrections of the fifth column are obtained. The resulting corrected values of the transference number for potassium ion are given in the sixth column, and are shown graphically in Fig. 3.

Shedlovsky[15] has shown that his semi-empirical extension to the limiting Onsager equation for conductivity fits the experimental data for many electrolytes remarkably closely, and Longsworth[16] has used an analogous equation to represent his transference numbers. For a 1–1 valent electrolyte, Longsworth gives

$$t_+ = t_+^\circ - \frac{1-2t_+^\circ}{\Lambda'} \cdot \beta\sqrt{C} + AC\left(1+\frac{2\beta\sqrt{C}}{\Lambda'}\right). \quad (1)$$

Here C is the concentration, t_+° is the transference number of the cation at infinite dilution, $\Lambda' = \Lambda_0 - (\alpha\Lambda_0 + 2\beta)\sqrt{C}$, Λ_0 is the equivalent conductance of the solution at infinite dilution (114.37 for potassium acetate at 25°), and α and β have their theoretical values for 1–1 electrolytes in aqueous solution at 25°C *viz.* 0.2274 and 29.90, respectively; A is a disposable constant. If $t_+^{\circ\prime}$ be written for $t_+^\circ + AC$, Eq. (1) is equivalent to

$$t_+^{\circ\prime} = (t_+ \cdot \Lambda' + \beta\sqrt{C})/(\Lambda' + 2\beta\sqrt{C}). \quad (2)$$

Hence, a plot of $t_+^{\circ\prime}$ against C should be a straight line whose slope is A, and whose intercept at $C=0$ is t_+°. Fig. 4 shows the result of such a plot; except for the highest concentration, the points lie on a straight line for which $A = -0.105_4$ and t_+° is 0.6428, as determined by the method of least squares. The last column of Table I and the continuous curve of Fig. 3 give the values of t_+ computed from Eq. (1) with these values of A and t_+°; Table II gives values of t_+ for a few round values of the concentration, and the straight line of Fig. 3 shows the limiting Debye slope. The discrepancy between the calculated and observed values of t_+ for the highest concentration is not surprising, since this concentration lies somewhat above the range where the Shedlovsky-Longsworth equation would be expected to hold; on the other hand, with such a strong solution, a relatively high current must be used, and consequently part of this discrepancy may be simply experimental error due to heating of the solution.

TABLE II.

C	0.01	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16
t_+	0.6498	0.6523	0.6556	0.6579	0.6596	0.6609	0.6620	0.6629	0.6636

MacInnes, Shedlovsky and Longsworth[14] give as the mobilities of potassium and acetate ion at infinite dilution at 25°, 73.50 and 40.87, values which they obtained from a consideration of the transference and conductance data for a number of electrolytes; the corresponding value of t_+° is 0.6427. The fact that the transference number obtained here is in such very close agreement is further evidence, if any were needed, of the essential correctness of their assignment of limiting ionic mobilities.[17] In conclusion, we wish to express our thanks to Mr. R. W. Allgood for assistance in calibrating one of the cells.

[15] Shedlovsky, J. Am. Chem. Soc. **54**, 1405 (1932).
[16] Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932).

[17] MacInnes, Shedlovsky and Longsworth's value for acetate ion was obtained by subtracting from MacInnes and Shedlovsky's limiting equivalent conductance for sodium acetate 90.97 (see reference 10) the limiting mobility of sodium ion, 50.10, which is known from their work to a high degree of precision; the extrapolation of the conductance to infinite dilution was effected by the Onsager-Shedlovsky equation. A recalculation of the disposable constants by the method of least squares from MacInnes and Shedlovsky's data shows, however, that the equation

$$\Lambda = 90.93_5 - 80.47C^{1/2} + 101._1C(1-0.2274C^{1/2})$$

fits their experimental values more closely than does the equation they employ. With $\Lambda_0 = 90.94$, the limiting ionic mobility for acetate ion will be 40.84, and the value of t_+° for potassium acetate 0.6428; this change in the transport number is of course quite insignificant.

The Density of Energy States in Solids

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(Received June 4, 1938)

FOR crystals or very complex molecules the energy levels are numerous and are either inherently or instrumentally unresolvable. As yet little progress has been made in devising methods of locating these levels although such information is of importance to any theory of molecular structure. In this note I wish to point out that a very general approach is available through the use of thermodynamic functions of the aggregate; further, to demonstrate that solutions exist for such equations which are experimentally indistinguishable from the ones specified by the data.

The sum-over-states may be readily computed from the entropy,

$$\log Z(T)=\frac{1}{kT}\int_0^T S(T)dT,$$

while
$$Z(T)=\sum_m g_m e^{-E_m/kT} \qquad (1)$$

is a fundamental definition of quantum statistical mechanics. The problem is reduced to an inversion of (1) so that $g_m(E_m)$ could be found once a $Z(T)$ is given. Clearly a rigorous solution is impossible even if the sum-over-states were known for all temperatures since, as $T\to\infty$, $Z(T)\to\infty$ very rapidly (in the order of T^N). Several of a number of possible approximations are briefly discussed below.

A. The function $Z(T)$ is continuous, finite, single valued and specified over the region $(0, T_1)$. However, it may have a discontinuous first derivative at temperatures at which the substance undergoes a change of phase. One may therefore approximate it to within any prescribed accuracy by a polynomial in T in the above range.

$$Z(T)=\sum_n a_n T^{n+1}, \quad Z(0)=0.$$

The change of variable $T=1/s$ results in

$$Z(1/s)=Y(s)=\sum_n a_n(1/s)^{n+1}$$

so that $Y(s)$ is analytic in the interval (s^1, ∞). Now, Eq. (1) may be rewritten in the form

$$Y(s)=\int_0^\infty g(E)e^{-sE/k}dE \qquad (2)$$

where $g(E)$ is the desired density function. The change from the sum to the integral is permissible because of the closely spaced energy levels. Since for all s whose real part is positive

$$(1/s)^{n+1}=\int_0^\infty e^{-sE/k}E^n/(n!k^{n+1})dE,$$

Eq. (2) is satisfied by

$$g(E)=\sum_n a_n E^n/(n!k^{n+1}) \quad \text{for } s\geqslant s_1.$$

Therefore a solution for (2) exists for all $s\geqslant s_1$.

B. If the range $0\leqslant s\leqslant\infty$ is desired, an equation approximating (2) must be treated. Introduce the function

$$Y(s+s_1)=\sum_n a_n(1/s+s_1)^{n+1}$$

which is analytic for $s\geqslant 0$. The necessary and sufficient conditions that a solution for

$$Y(s+s_1)=\int_0^\infty kg(E)e^{-s(E/k)}d(E/k) \qquad (3)$$

exists are then satisfied (inversion by means of the Laplace transform[1]). It follows that if the maximum temperature for which $Z(T)$ is known is large—i.e. s_1 is sufficiently small—so that $Y(s+s_1)$ may be identified with $Y(s)$ to within the accuracy of the data, that solution could be accepted also for (2). One should keep in mind that often for $T\gg\theta$, a safe extrapolation of $S(T)$ to larger T may be made.

C. Write Eq. (1) in the form

$$Z(T)=\int_{E_0}^{\beta kT} g(E)e^{-E/kT}dE;$$

E_0 describes the ground state. The approximation enters in replacing the upper infinite limit by

[1] D. V. Widder, Trans. Am. Math. Soc. **36**, 116 (1934).

βkT where β is a very large number, of such magnitude as to make $\int_{\beta kT}^{\infty} g(E)e^{-E/kT}dE$ negligible. A change of variable $\beta kT=t$ transforms the above into a Volterra integral equation of the first kind,

$$Z(t/\beta)=\int_{E_0}^{t} g(E)e^{-\beta E/t}dE \qquad (4)$$

with $E_0 \leqslant E \leqslant t \leqslant \beta kT_1$. Integration by parts or a differentiation leads to an equation of the second kind for which a unique continuous solution exists, in the latter case provided $Z(E_0/\beta)=0$.[2] This will be almost true if β is taken sufficiently large; actually, the solution found will be for the equation

$$\mathbf{Z}(t/\beta)-\mathbf{Z}(E_0/\beta)=\int_{E_0}^{t} g(E)e^{-\beta E/t}dE,$$

where $\mathbf{Z}=Z$ except in that the discontinuities in the derivative of Z if there are any, have been smoothed over.

I have undertaken the application of these suggestions to the case of diamond for which accurate specific heat data have recently been published.[3] Pitzer found that the experimental curve lies between the one predicted using the continuous solid model and that deduced from the three-dimensional lattice theory of Blackman.

[2] G. Kowalewski, *Integralgleichungen* (Gruyter, 1930).

[3] K. S. Pitzer, J. Chem. Phys. **6**, 68 (1938).

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A Note on the paper by J. N. Pearce and Lyle R. Dawson on "The Influence of Salts on the Absorption Spectra of Aqueous Cobalt Chloride Solutions"

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(Received May 16, 1938)

SINCE in the recent paper of J. N. Pearce and Lyle R. Dawson,[1] the inadequacy of existing explanations of the well-known color changes in cobalt chloride solutions has been mentioned, the present author wishes to show that his explanation put forward eight years ago[2] cannot be regarded as an unsatisfactory one for the experiments given by the above named authors.

The explanation of the present author is based on a polarigraphic study of current-voltage curves obtained in electrolysis of cobalt chloride solutions with the dropping mercury cathode, as well as on spectroscopic research. Through these investigations it has been proved that cobalt deposits at the dropping mercury cathode from blue solutions with a large concentration of calcium chloride at a more positive potential than it does from the pure pink water solutions. Further, while the current-voltage curves in the latter case do not conform to the expected equation for the deposition of a divalent metal, the deposition from the blue cobaltous solutions proceeds according to this equation. The deviation from this equation has been explained as being due to the slowness of dehydration of cobaltous ions, which takes place at the surface of the cathode in order to deposit metallic cobalt. The easier deposition from blue solutions in which a blue complex $[CoCl_n]^{(n-2)-}$ has to be assumed, is imagined to be facilitated by the ease of splitting of such a complex into free cobaltous ions.

These facts led the present author to the conclusion that the effect of the addition of a large excess of calcium chloride in the hydrated pink cobaltous ions is twofold: 1. The activity of water is lessened and thus the concentration of dehydrated cobaltous cations is increased, 2. the

[1] J. N. Pearce and Lyle R. Dawson, J. Chem. Phys. **6**, 128 (1938).

[2] R. Brdička, Coll. Czechoslov. Chem. Comm. **2**, 489 and 545 (1930).

dehydrated cations on the other hand associate with chloride anions to form complexes like $[CoCl_n]^{(n-2)-}$ according to the equilibrium

$$Co^{\cdot\cdot} + nCl^- \rightleftarrows [CoCl_n]^{(n-2)-}.$$

This can serve as a satisfactory explanation of the findings of Pearce and Dawson, according to which equimolal high concentrations of added chlorides do not produce equal color changes. In accordance with the author's view quoted above, the concentration of the complex depends primarily on the dehydrating power of the cation added (i.e., on its ionic charge and its ionic volume) and the complex formation proceeds thus parallel with the dehydration of cobaltous ions. This would correspond to some extent with the explanation given recently by Pearce and Dawson who stated: "As strong hydrating ions are added, they attract and orient solvent molecules. At high concentration of the added salt much of the solvent envelope about the cobalt ions is removed. Cobalt and chloride ions are then drawn more closely together by electrostatic attraction."

No doubt however, can be cast upon the theory that complex ions of the type $CoCl_4^{--}$ are formed, since the existence of such particles has been sufficiently justified by the electrolytic transfer at which cobalt present in blue solutions migrates towards the anode.[3-6]

As to the mechanism of the light absorption of the cobalt chloride solutions in the green and red part of the spectrum, no experimental evidence has been brought forward by the named authors which could prove that the absorption is due to the electronic transition in the unfilled third quantum group of cobalt. In this respect more satisfactory measurements have been given by W. R. Brode and R. A. Morton.[7, 8]

The statement of Pearce and Dawson that chloride anions distort the electronic system of the cobalt ion in such a way that the electrons in the third quantum group are capable of absorbing smaller quanta of energy, is by no means less hypothetical than the original conclusion of the present author, who ascribes the color change to the bond of chloride anions in the coordinative sphere of cobalt by which the outer electronic shell of Cl^- ions is supposed to be deformed.

If one takes into account that the two electrons of such a deformed outer electronic shell of chloride anions are really a part of the electronic system belonging to cobalt, one could equally accept that the absorption is due just to this electron pair supplied to the cobalt by Cl^- ion.

Finally, the present author wishes to correct the following statement used by Pearce and Dawson wrongly ascribed to him, *viz.:* "That such color changes could be due to the deformation of the chloride ions (cited by R. Brdička) by strongly hydrating cations. . . ." The deformation of chloride anions was explained in the original paper of the present author as being due to the bond with the cobalt central atom, but never as being effected by strongly hydrating cations.

[3] F. G. Donnan and H. Bassett, J. Chem. Soc. **81**, 939 (1902).
[4] H. G. Denham, Zeits. f. physik. Chemie **65**, 641 (1909).
[5] J. Gróh, Zeits. f. anorg. allgem. Chemie **146**, 305 (1925).
[6] J. Gróh and R. Schmid, Zeits. f, anorg. allgem. Chemie **163**, 321 (1927).

[7] W. R. Brode, Proc. Roy. Soc. **A118**, 286 (1928).
[8] W. R. Brode and R. A. Morton, Proc. Roy. Soc. **A120**, 21 (1928).

Note on the Heat Capacities and Energies of $SiCl_4$, $TiCl_4$ and $SnCl_4$

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(Received June 10, 1938)

THE interest in thermodynamic functions calculated from spectroscopic data is the reason for tabulating some information that has been available to us for some time. The heat capacities and energies of $SiCl_4$, $TiCl_4$ and $SnCl_4$ were calculated by means of well-known formulae.[1] The frequencies (liquid) employed were taken from Kohlrausch[2] and are given in Table I along with their degeneracies in parentheses. Since the molecules investigated are nonpolar there should be no great difference in the calculated functions if we employ the frequencies obtained from the liquids rather than the gases. In fact, for gaseous $SnCl_4$ the frequencies ν_1 and ν_3 are 367 and 400 cm^{-1} [3] as compared to 367 and 401 cm^{-1} for the liquid. The heat capacity in cal./mole deg. for each gas in its standard state is tabulated in Table II and in Table III we have tabulated the energies in cal./mole. Since these molecules have low frequencies and anharmonicity corrections are not available, the calculation was not carried beyond 300°C. Table IV gives the only experimental heat capacity data[4] that could be found for these tetrachlorides in the gaseous phase and as can be seen the calculated values agree fairly well. The ice point on the Kelvin scale has been taken as 273.1°K and the fundamental constants employed were those given by Birge.[5]

TABLE I.

	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
$SiCl_4$	422 cm^{-1}	148 cm^{-1}	608 cm^{-1}	220 cm^{-1}
$TiCl_4$	386	119	491	139
$SnCl_4$	367	104	401	136

TABLE II. *Heat capacities in cal./mole deg.*

T°C	$SiCl_4$		$TiCl_4$		$SnCl_4$	
	C_{vib}	C_p	C_{vib}	C_p	C_{vib}	C_p
0	13.19	21.14	14.50	22.45	15.24	23.19
10	13.41	21.36	14.68	22.63	15.39	23.34
20	13.63	21.58	14.85	22.80	15.53	23.84
30	13.83	21.78	15.01	22.96	15.66	23.61
40	14.02	21.97	15.16	23.11	15.78	23.73
50	14.20	22.15	15.29	23.24	15.90	23.85
60	14.37	22.32	15.42	23.37	16.00	23.95
70	14.52	22.47	15.54	23.49	16.09	24.04
80	14.68	22.63	15.65	23.60	16.19	24.14
90	14.81	22.76	15.75	23.70	16.26	24.21
100	14.94	22.89	15.85	23.80	16.34	24.29
200	15.92	23.87	16.55	24.50	16.89	24.84
300	16.48	24.43	16.94	24.89	17.19	25.14

TABLE III. $E^0-E_0^0$ *cal./mole.*

T°C	$SiCl_4$	$TiCl_4$	$SnCl_4$
0	3576	4031	4217
20	3962	4444	4645
50	4557	5075	5294
100	5583	6152	6400
200	7726	8377	8664
300	9936	10650	10970

TABLE IV.

	T°C	C_p cal./mole deg.
$SiCl_4$	90–234	22.5
$TiCl_4$	136–271	24.5
$SnCl_4$	149–273	24.5

[1] For instance, see Fowler, *Statistical Mechanics* (Macmillan, 1936).
[2] Kohlrausch, *Der Smekal-Raman-Effekt* (Berlin, 1931).
[3] Braune and Engelbrecht, Zeits. f. physik. Chemie **B19**, 303 (1932).
[4] Regnault, Mém. de l'Acad. **26**, 1 (1862).
[5] Birge, Phys. Rev. Sup. **1**, 1 (1929).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Hindered Internal Rotation of Ethane

We have further improved the "hot wire" gaseous heat capacity apparatus of Kistiakowsky and Nazmi,[1] eliminating possible errors due to gas adsorption and "end conductance." Measurements on C_2H_6 and C_2D_6 near liquid oxygen temperature show that the observed heat capacity is independent of the nature of the wire, of the gas pressure, and of the temperature difference between the wire and the surrounding wall. The vibrational heat capacity of C_2H_6 at these temperatures is negligible, and that of C_2D_6 is certainly less than 0.05 cal./mole deg. By subtracting the vibrational, over-all rotational, and translational heat capacities from our measured values, we find for C_2H_6 the contribution of the hindered internal rotation to be 0.59 and 0.67 cal./mole deg. at 94° and 100°K. For C_2D_6 similarly we find 1.03 and 1.13 cal./mole deg. at 94° and 100°K. The values for light ethane are to be compared with Hunsmann's[2] data: 0.40 at 95° and 0.56 at 101°.

The theoretical dependence of the hindered internal rotational heat capacity upon the assumed magnitude of a restricting potential of the form $(1/2)V(1-\cos 3\theta)$ is shown in Fig. 1 for the temperatures in question. It will be seen that a barrier of about 3000 cal./mole is the only assumption consistent with the experimental data, provided this method of calculation[3] is not invalidated by quantum effects due to the existence of nuclear spin isomers—a point raised by Hunsmann.[2] In the following letter Professor Wilson reports that these quantum effects are completely negligible at these temperatures. It follows that the low temperature gaseous heat capacity of ethane cannot be interpreted in terms of a low potential barrier and these quantum effects as suggested by Hunsmann, but requires instead a high restricting barrier as indicated above. It also follows that the agreement of the entropy calculated semi-statistically by Hunsmann (i.e., statistically for over-all rotation and translation but graphically for the internal degrees of freedom) with the third law value is not accidental, as he suggests, but is a direct consequence of the existence of the high barrier. On the other hand the poor agreement of Hunsmann's calculated heat capacity of C_2H_6 for a high barrier with the experimental points between 100° and 200°K is due to an inadequate method of calculation. Using the hindered rotator model with $V=3000$ cal./mole, satisfactory agreement between theory and experiment is obtained over the entire temperature range for which the experimental data exist, provided the uncertain vibrational frequency in C_2H_6 is taken to be between 1000 and 1200 cm^{-1}. This frequency is not in accordance with Bartholomé and Karweil's[4] vibrational analysis, a point which will be discussed in papers soon to appear from this laboratory.

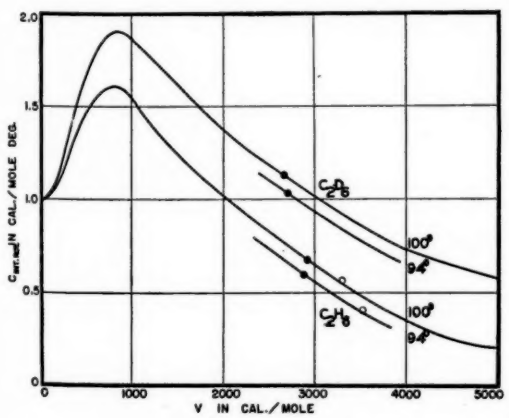

FIG. 1. Internal rotational heat capacity of ethane as a function of potential barrier. Filled circles, this work. Open circles, Hunsmann.

Thus, in addition to the other thermodynamic[5] and spectroscopic[6] evidence[7] for the existence of a fairly high barrier hindering internal rotation in ethane, the low temperature gaseous heat capacity leads directly to the conclusion that this barrier must be of the order of magnitude of 3000 cal./mole, without any other alternative.

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[1] G. B. Kistiakowsky and F. Nazmi, J. Chem. Phys. **6**, 18 (1938).
[2] W. Hunsmann, Zeits. f. physik. Chemie **B39**, 23 (1938).
[3] K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937).
[4] E. Bartholomé and J. Karweil, Zeits. f. physik. Chemie **B39**, 1 (1938).
[5] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **58**, 137 (1936); J. D. Kemp and K. S. Pitzer, ibid. **59**, 276 (1937).
[6] J. B. Howard, J. Chem. Phys. **5**, 451 (1937).
[7] This evidence has not been generally regarded as conclusive. See Kassel, J. Am. Chem. Soc. **59**, 2745 (1937).

Absence of Spin Effects in the Heat Capacity of Ethane Gas

Hunsmann[1] has suggested that the low value of the heat capacity of ethane gas at 100°K does not necessarily prove the existence of a high potential barrier in this molecule because of the possibility that the calculations have been incorrectly made, since no consideration was taken of the fact that there are several noncombining nuclear spin species, analogous to ortho- and parahydrogen. Because of the relatively large moment of inertia of ethane, this suggestion seemed inherently unreasonable, but on account of the importance of this problem, a detailed calculation of the partition function and heat capacity of each of the spin species of ethane has been made for several different barriers and temperatures, in which full account was taken of the statistical weights of each individual rotational energy level. The method used to find these weights was an extension of that described earlier for the general problem.[2] The rotational group for ethane has 18 elements and 9 irreducible representations. Some of these occur as conjugate pairs, however, so that there are only six possible spin species of ethane. At 90°K the over-all rotation of the molecule is classically excited with the result that these six species can be divided into two sets, the members of each set having the same partition functions. The partition function for one set involves the state sum over those levels of the internal motion which are nondegenerate, while the partition function for the other set involves the sum over the degenerate levels of the internal torsional motion. For very high barriers the levels of the two species become identical and for very low barriers the levels go over into those for free rotation. In each of these limiting cases the two partition functions are negligibly different at 90°K. A detailed calculation for a barrier of 300 cal. yields the same result. This means that the equilibrium proportions of the two species have practically attained their high temperature limiting values at 90°K. Furthermore the heat capacities of the two species are identical at this temperature or higher. Consequently, the usual method[3] of calculation which involves the neglect of spin and symmetry effects is entirely justified.

This eliminates one possible explanation of the heat capacity of ethane gas at low temperatures and seems to leave the existence of a high barrier as the only alternative.

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[1] W. Hunsmann, Zeits. f. physik. Chemie **B39**, 23 (1938).
[2] E. B. Wilson, Jr., J. Chem. Phys. **3**, 276 (1935); L. S. Kassel, Chem. Rev. **18**, 277 (1936).
[3] K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937).

Carbon Isotope Effect in the Raman Spectrum of Dimethylacetylene

For dimethylacetylene Glockler and Davis[1] reported a pair of strong Raman frequencies, 2235 and 2313 cm^{-1} which were accompanied by two overlapping pairs of weak lines, 2201 and 2280 cm^{-1}, 2179 and 2258 cm^{-1}, all excited by Hg 4358A. (Fig. 1.) They divided these lines into two

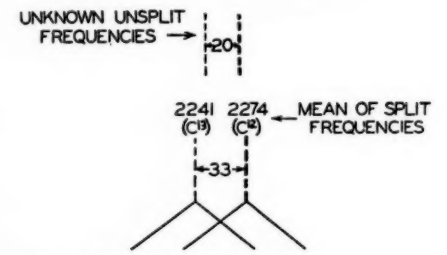

FIG. 1. Raman frequencies of the triple bond in dimethylacetylene (cm^{-1}).

groups, one consisting of the higher members of the pairs, the other of the lower frequency members. Each group was considered to represent a strong vibration accompanied by weaker components which were the first members of *P* rotation series. Such a lopsided rotation-vibration band had been proposed by Bonino and Cella[2] to account for a similar group of lines in α-pinene. In both substances excellent checks on observed separations were obtained by assuming that the rotating portions of the molecules were simple rotators with one degree of freedom. In dimethylacetylene it was assumed that the six hydrogen atoms were rotating about the figure axis.

Of course there were objections to the above interpretation. The restricted nature of the rotator calculations and the absence of *R* branches caused doubt. Recently in studies conducted here on other low molecular weight hydrocarbons[3] measurements were made on the weak Raman shifts due to molecules containing the C^{13} isotope. In continuing this study reference was made to the available plates on dimethylacetylene in a search for lines of isotopic origin. The first pair of weak lines listed, giving a separation of 33 cm^{-1} from the corresponding members of the strong pair, were considered to be due to molecules containing C^{13}.

The elimination of the first component in each rotation series necessitated another explanation for the other members. It was then found that the 2179 and 2258 cm^{-1} weak lines were exactly in position to be the 2235 and 2313 cm^{-1} strong shifts excited by the 4347.5A member of the mercury triplet. In the paper mentioned no further weak lines were reported; however, in an enlargement of one of the plates by Davis a faint line was discernible which was in position to be the 2235 cm^{-1} shift excited by the 4339.2A member of the triplet; the 2313 cm^{-1} shift thus excited would not be visible because of coincidence with a strong line. In consequence of these measurements the rotational interpretation of the faint lines is to be discarded.

Subsequent to the studies of Glockler and Davis the

pair of strong lines, 2235 and 2313 cm^{-1} were explained by Badger[4] as manifestations of a single fundamental vibration interacting with an overtone of a lower fundamental in Fermi resonance due to accidental degeneracy. As a result, this carbon-carbon triple bond vibration frequency of the normal molecule appears split into two components, the actual fundamental frequency lying near the mean value of the pair. Similarly the weak pair of lines, 2201 and 2280 cm^{-1}, are now considered to result from the interaction of the carbon-carbon triple bond fundamental of isotopic molecules with an overtone of a lower fundamental of these isotopic molecules.

By considering the normal molecule to be a simple harmonic two-body oscillator with reduced mass of $1/\mu=1/25+1/25$ and the isotopic molecule to have similar properties with a reduced mass of $1/\mu=1/25+1/26$ it is possible to calculate a separation of 20 cm^{-1} for the carbon-carbon triple-bond frequencies of the normal and the isotopic molecules. This is not checked very well by the experimental measurement of 33 cm^{-1} separating the mean values of the resonance split pairs. Of course this calculation is only an approximation. However, it must be emphasized that a close check is not to be expected since the separation of mean values of split frequencies does not give an accurate measure on separations of the "unsplit" carbon-carbon triple bond frequencies. The resonance split values observed depend not only on the "unsplit" fundamentals but also on the overtone of the lower fundamentals likewise engaged in the resonance interaction.[5] Because the isotopic shift for the lower frequency will differ from that for the higher frequency, the separation of mean values of split frequencies necessarily will vary from the separation of the true, "unsplit" fundamental vibrations in normal and isotopic molecules.

In the present approximate treatment no consideration was given to location of the C^{13}. In dimethylacetylene roughly four percent of the molecules are isotopic with half of these having isotopic triple bond carbons, the other half possessing C^{13} in the methyl groups.

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[1] G. Glockler and H. M. Davis, J. Chem. Phys. **2**, 881 (1934).
[2] G. B. Bonino and P. Cella, Nature **126**, 915 (1930).
[3] G. Glockler and M. M. Renfrew, J. Chem. Phys. **6**, 340 (1938).
[4] R. M. Badger, J. Chem. Phys. **5**, 178 (1937).
[5] G. Placzek, *Handbuch der Radiologie*, Vol. 6 (Akad. Verlagsges. Leipzig, 1934), p. 326.
[6] M. M. Renfrew, du Pont Fellow (1937–38).

Raman Effect in Liquid Ethylene and Ethane

In the Raman spectrum of liquid ethylene two lines, 943 and 3075 cm^{-1} have been observed[1] which have not been found in the gas on very long exposures at high pressure.[2] Since the work of Bonner[3] on Raman effect in the liquid and infra-red absorption in the gas, it has been customary in theoretical treatments[4] to use these lines (950 and 3069 cm^{-1}) as fundamental vibrations along with other frequencies including 940, 950, and 3107 cm^{-1} which are infra-red active. According to the selection rules derived for gases,[5] in molecules having a center of symmetry frequencies which are infra-red active should not appear in Raman effect. Of course there exists the possibility of an accidental coincidence of values. However, it is our belief that the appearance of the two lines mentioned in the Raman spectrum of liquid ethylene constitutes a violation of the selection rules since it seems likely that similar values in the infra-red absorption spectrum arise from the same vibrations.

The 3075 cm^{-1} line is somewhat diffuse but is of such a strength that it certainly should be visible on reasonable exposures in the gas, if permitted there. The line cannot be interpreted readily as a combination or overtone. Hence it seems convenient to relate this line to the strong 3107 cm^{-1} vibration observed in the infra-red. Of course, some increase in value is expected in going from liquid to gas for high frequencies. The increase here seems large, but does not appear excessive.

The 943 cm^{-1} shift in Raman effect for the liquid is very diffuse, and it seems natural to identify this with the 940 and 950 cm^{-1} lines in the infra-red. For low frequencies no great drop in value is observed generally in passing from gas to liquid.

Moreover, a similar comparison of data is possible with the Raman spectrum of liquid ethane and its infra-red absorption spectrum for the gas. In pure liquid ethane the Raman line 1463 cm^{-1}, though diffuse, is well established.[6] However, in the gas Lewis and Houston[7] could not find it and although Bhagavantam[8] measured a shift in this neighborhood he was using an impure sample and considered the line observed to be due to a contaminant. Now in infra-red absorption experiments[9] strong bands are observed at 1465 and 1495 cm^{-1}. Perhaps the mean value of 1480 cm^{-1} for the gas corresponds to the 1463 cm^{-1} Raman shift observed in the liquid.

In addition there are indications of a faint, diffuse Raman shift of 813 cm^{-1} in liquid ethane which may be related to the infra-red band 827 cm^{-1}.

Now it is possible that the failure to observe these Raman lines in the gas is due to their low intensities. But other lines of comparable strength (frequently of lower intensity) have been recorded in the gas. For this reason it seems likely that the Raman lines discussed are permitted only in the liquid state. The shifts are of nearly the same magnitude as infra-red active frequencies (see Table I), which fact may not be accidental. The presence of the C^{13} isotope has been shown to be responsible for slightly altered Raman shifts of low intensity accompanying corresponding strong lines excited in the normal molecules. The presence of this isotope contributes a small degree of asymmetry to the molecules which would cause infra-red active frequencies to be permitted in the Raman effect. However, such manifestations should be visible on long exposures in the gas as well as in the liquid. Since this condition has not been observed, it seems more reasonable to suppose that if the Raman and infra-red frequencies do belong to identical fundamentals, then a breakdown in selection rules in the liquid state for certain lines is indicated and must be due to the more strenuous environment existing there. Thompson and Linnett[4] have offered this

TABLE I.

SUBSTANCE	INFRA-RED (GAS)	RAMAN EFFECT (LIQUID)	RAMAN EFFECT (GAS)
Ethylene	940 >945 950	943	not found
	3107	3075	not found
Ethane	827	813	not found
	1465 >1480 1495	1463	? (8)

suggestion in the case of ethylene, but for purposes of comparing calculated values with experimental data they considered the Raman lines in question to be bona fide Raman active fundamentals. Our experience adds weight to their tentative objections for the ethylene lines. Moreover, data given for ethane are substantiating. Perhaps theoretical treatments of the ethylene molecule will profit by including among the Raman active fundamentals one or both of the high frequency values, 3230 and 3263 cm^{-1}, whose existence we have verified.[1]

Recently we have made more accurate evaluations on our plates for the Raman spectrum of liquid ethylene, resulting in slight alteration of previously published values.[1] The new measurements are: 943 (1*d*), 1341 (10), 1602 (0.5), 1621 (7), 1653 (1), 2870 (2), 2997 (0.5), 3008 (10), 3075 (2*d*), 3230 (0.5), 3263 (0.5). The estimated intensities are in parentheses.

The 1602 cm^{-1} shift is the carbon-carbon vibration in the isotopic molecule $H_2C^{13}=C^{12}H_2$. The shift 2997 cm^{-1} probably also is due to this isotopic molecule, the separation from the 3008 cm^{-1} vibration of the normal molecule being checked roughly by calculation. However, the accuracy of measurement has been diminished by the lack of clear resolution of the weak and strong line. Our value for the isotope line probably is low.

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[1] G. Glockler and M. M. Renfrew, J. Chem. Phys. **6**, 170 (1938).
[2] S. Bhagavantam, Nature **138**, 1096 (1936).
[3] L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936).
[4] H. W. Thompson and J. W. Linnett, J. Chem. Soc. 1376 (1937). C. Manneback and A. Verleysen, Ann. soc. sci. de Bruxelles **56B**, 349 (1936).
[5] G. Placzek, *Handbuch der Radiologie*, Vol. 6, Akad. Verlagsges (Leipzig 1934), p. 305.
[6] G. Glockler and M. M. Renfrew, J. Chem. Phys. **6**, 295 (1938).
[7] C. M. Lewis and W. V. Houston, Phys. Rev. **44**, 903 (1933)
[8] S. Bhagavantam, Ind. J. Phys. **6**, 596 (1931).
[9] E. Bartholomé and H. Sachsse, Zeits. f. physik. Chemie **30B**, 40 (1935).
[10] M. M. Renfrew, du Pont Fellow (1937–38).